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RESEARCH PAPER RP743

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CALIBRATIONS OF THE LINE STANDARDS OF LENGTH OF THE NATIONAL BUREAU OF STANDARDS

Lewis V. Judson and Benjamin L. Page

ABSTRACT

The results of the intercomparison of total lengths of meter and of decimeter bars, and the results of calibrations of subintervals of several of them are given in considerable detail. The precision of the results is discussed. That the basis of length measurements in this country (United States Prototype Meter 27) has remained unaltered to about a part in 10,000,000 for over 40 years is pointed out, and the wisdom of the conclusions stated by Louis A. Fischer in the first scientific paper published by the Bureau is shown.

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I. THE LINE STANDARDS OF LENGTH

Three groups of line standards of length are discussed in this paper, namely, platinum-iridium prototype meters, nickel-steel meters, and decimeters. By a line standard is meant a standard in which the length is defined as the distance between lines or graduations on the surface. Thus the platinum-iridium prototype meters are standards in which the meter, as a unit of length, is the nominal distance between specified lines on these bars. Such terms as meter and decimeter are commonly used to designate either a standard or a unit. Which of these two meanings is intended must be clear from the context. A complete calibration of a line standard involves a determination of its length at one temperature, a determination of its thermal expansivity, and a series of measurements to determine the corrections to subdivisions.

Instead of giving the length of a standard, it is more convenient to state the correction. The actual length is equal to the nominal length plus the correction. Hence a plus correction indicates that a standard is longer than the nominal length.

Unfortunately, the length of a standard at a specified temperature cannot be assumed to remain the same indefinitely, because the "aging" of metals commonly involves structural changes which alter the length. If these changes are not uniform throughout the length, a calibration of the subintervals of a standard before the changes took place will not give the true lengths afterward. A fundamental part of the work of the length-measuring laboratory of a national standardizing bureau is the repeated calibration of its standards so as to maintain the requisite accuracy at all times. An account of some of this work forms the basis of this paper.

1. PLATINUM-IRIDIUM METER BARS

The National Bureau of Standards (NBS) has four platinum-iridium meter bars obtained from the Bureau International des Poids et Mesures (BIPM) and certified by that Bureau. One of these, United States Prototype Meter 27, is considered to be the primary standard of length in the United States. Meter 21 is the meter bar most frequently used in determining the total length of the laboratory standards of length of the NBS. Meters 12 and 4, both of the "Alloy of 1874", have been used in less important comparisons and as checks. Meter 4 is subdivided and has been used considerably in standardizing lengths of less than a meter.

All of these bars are of the same X-shape as the International Prototype Meter.[1] With the exception of meter 4, which is subdivided to millimeters, each of these bars has near each end a group of three transverse lines intersected by two longitudinal lines. Measurements are made on the central one of each group of transverse lines, using that part of the line between the two longitudinal lines.

The lengths of these meters were determined at the BIPM before the bars were sent to this country. Meter 4 was received in 1907; the other three in 1890. Meter 27 was recompared at the BIPM in 1903 and again in 1922–23. Meter 21 was recompared there in 1932.

For a number of years the BIPM has been engaged in making two extensive series of measurements, one to determine the values of the coefficients of thermal expansion of the platinum-iridium meters more accurately than was possible when the original certificates were issued; the second, to obtain new intercomparisons of the total lengths of a large number of these meter bars. As a result of this work, new corrections at 0 ° C and new coefficients of expansion were authorized by the Eighth General (International) Conference on Weights and Measures which met in Paris in 1933. In the case of meters 12 and 4 of the Alloy of 1874 which had not been returned to the BIPM the new values merely correct the computations made at the time of the original measurements, using the new coefficients and, in the case of meter 4, employing the probable value of laboratory standards used at the BIPM in 1907.

The values in the original certificates and also the new values are given in table 1.

[1] For a more detailed description see p. 2 of BS Circular 332; p. 742 of Appendix 18, Report of USC&GS for 1890; or publications of the BIPM.

TABLE 1.—*Data concerning the meter and decimeter bars*

Length of bar at temperature T=[nominal length+correction at 0°C] × [1+(coefficient of expansion) × T°]

NOTE.—Meters 27 and 21 are of the principal national series of prototypes; meters 12 and 4 are of the alloy of 1874; meters 39,153 R and 354 have serial numbers of the Société Genevoise. Meter 153 R has an inlaid strip of platinum for the graduations.

1	2	3	4	5	6	7	8	9	10
Designation of bars	Composition	Authority	Date	Correction at 0°C	Coefficient of expansion [b]	Authority	Date	Correction at 0°C	Coefficient of expansion
Meter:				μ				μ	
27	Platinum-iridium	BIPM	1889	−1.6	$(8.657+0.00100\ T)10^{-6}$	BIPM	1933	−1.47	$(8.6210+0.00180\ T)10^{-6}$.
21	do	BIPM	1889	+2.5	$(8.665+0.00100\ T)10^{-6}$	BIPM	1933	+3.42	$(8.6210+0.00180\ T)10^{-6}$.
12	do	BIPM	1889	+3.3	$(8.634+0.00100\ T)10^{-6}$	BIPM	1933	[a] +3.34	$(8.6014+0.00180\ T)10^{-6}$.
4	do	BIPM	1907	−5.9	$(8.655+0.00100\ T)10^{-6}$	BIPM	1933	[a] −5.13	$(8.6014+0.00180\ T)10^{-6}$.
39	Invar	NBS	1907	----------	1.48×10^{-6}	NBS	1913	----------	1.54×10^{-6}.
153 R	42-percent nickel steel	----------	----------	----------	----------	NBS	1914	----------	7.02×10^{-6}.
354	Invar	----------	----------	----------	----------	NBS	1924	----------	1.68×10^{-6}.
Decimeter:									
10	Invar	BIPM	----------	+2.0	$(0.965-0.00017\ T)10^{-6}$	BIPM	1929	----------	$(1.071-0.00181\ T)10^{-6}$.
20	do	BIPM	----------	−4.5	$(0.965-0.00017\ T)10^{-6}$	BIPM	1929	----------	$(1.071-0.00181\ T)10^{-6}$.
24	44-percent nickel steel	BIPM	1900	−1.8	$(8.298-0.00328\ T)10^{-6}$	BIPM	1929	----------	$(8.273-0.00251\ T)10^{-6}$.
43	Invar	BIPM	1900	−4.0	$(0.965-0.00017\ T)10^{-6}$	BIPM	1929	----------	$(1.071-0.00181\ T)10^{-6}$.
56	do	BIPM	----------	+.4	$(0.965-0.00017\ T)10^{-6}$	BIPM	1929	----------	$(1.071-0.00181\ T)10^{-6}$.
57	44-percent nickel steel	BIPM	1923	−6.0	$(8.298-0.00328\ T)10^{-6}$	BIPM	1929	----------	$(8.273-0.00251\ T)10^{-6}$.
61	Nickel	BIPM	1923	−3.2	$(12.540+0.00635\ T)10^{-6}$	BIPM	1929	----------	$(12.515+0.00712\ T)10^{-6}$.

[a] Value as recomputed from original observations prior to issuing original certificates.

[b] Certificates from the BIPM have given equations and temperatures on the basis of the normal hydrogen scale, while comparisons of length standards at NBS have been on the basis of the international temperature scale. These two scales are the same within the limits of reproducibility of the normal hydrogen scale. No distinction between the two temperature scales is made in this paper.

2. LABORATORY STANDARD METER BARS

At the NBS a group of meter bars of nickel steel, having the H-shape cross section, and made by the Société Genevoise d'Instruments de Physique, are used in many of the routine length comparisons. These bars are standardized by comparison with the platinum-iridium bars.

Two of these, meter 39 of invar and meter 153 R of 42 percent nickel steel with a dovetailed strip of platinum for the graduations, and also a meter, 354, of invar submitted to the NBS for test, are included in this intercomparison.

Meter 39 has had extensive use, and its decimeter intervals were used in the standardization of the decimeter bars described in this paper.

The coefficients of expansion determined for these bars are given in table 1.

3. DECIMETER BARS

The NBS has four decimeter bars obtained from the BIPM: a 44 percent nickel-steel bar, 24, and an invar bar, 43, both purchased in 1901, and a 44 percent nickel-steel bar, 57, and a pure nickel bar, 61, both purchased in 1923.

Three additional decimeter bars belonging to universities in this country were also made available for inclusion in the measurements. These bars are decimeter 10, belonging to Northwestern University; decimeter 20, belonging to Clark University; and decimeter 56, belonging to the University of Chicago.

Each of these bars has a rectangular cross section about 21 mm wide and 7 mm high, an extreme length of approximately 150 mm, a scale 100 mm long divided in millimeters, and a separate millimeter interval divided in tenths. The graduations are intersected by two longitudinal lines 0.2 mm apart, which define the part of the line to be used in making a micrometer setting.

The coefficients of thermal expansion given in the BIPM certificates for these decimeter bars were obtained in a test of 1-meter bars from the same melt, measurements being made at six different temperatures, ranging from 0 to 38° C. Since the certificates were issued, additional measurements have been made on the several 1-meter bars referred to above and new values for the coefficients reported. The lengths and both sets of coefficients are given in table 1.

According to the certificates, the errors of the divisions of these scales were determined by the aid of a longitudinal comparator especially constructed for that purpose. This comparator, constructed by Bariquand and Marre, is described in more detail in various publications of the International Bureau. In some of the calibrations, microscopes were used having a magnification of about 200, but in other cases the magnification was much less. The procedure for the measurements was this: After the scale had been placed in position in the comparator in alinement with another standard of the same metal, each of the centimeter intervals of the first standard was compared with each of the centimeter intervals of the second standard. Then each of the millimeter intervals of the first centimeter on one standard was compared with each of the millimeter intervals of the first centimeter of the second standard. The same procedure was followed for the intervals of the subdivided millimeter. This subdivided millimeter in turn was compared with 10 calibrated millimeter intervals of the auxiliary scale.

Observations at the NBS over a period of years on bars 24, 43, 57, and 61 indicated that the values certified by the BIPM were not consistent and that a complete intercomparison was advisable.

II. CALIBRATION OF THE METER BARS

The fundamental measurements in this work on the length standards were those made in 1928 in the intercomparison of the four platinum-iridium meters and invar meter 39. The results of an auxiliary comparison, made in 1930 primarily for another purpose, are included in this paper because they serve as a check on the earlier measurements. A subsidiary but important part of the work with the meter bars was the calibration of the invar meter to decimeters.

1. DETERMINATION OF TOTAL LENGTH

The intercomparison of the total length of the meter bars was undertaken at the NBS in 1928, using the new longitudinal comparator.[2] The bars were placed in the eight possible positions relative to each other, and 10 comparisons were made in each position at an average temperature of approximately 23° C. From these observations, values at 0° C were computed. As the recent BIPM determinations of coefficients of expansion for the platinum-iridium meter bars may be considered as fully meeting the needs of metrology, they may be used with confidence in reducing the above observations to 0° C. The results are given in table 2.

TABLE 2.—*Differences in length of meter bars at 0° C*

[1928 series of comparisons]

Observations made at temperature T and reduced to 0° C using values of the coefficients given in column 10 of table 1.
$A-B=\Delta L$.

Bars compared	Observed difference, ΔL	Probable error	Observed temperature, T
A B	μ	μ	°C
21 minus 27	+5.088	±0.048	22.27
12 minus 27	+5.049	±.042	22.58
4 minus 27	−3.958	±.042	22.90
39 minus 27	−40.544	±.040	22.22
12 minus 21	−.113	±.043	24.01
4 minus 21	−8.862	±.040	23.17
39 minus 21	−45.638	±.043	22.57
4 minus 12	−8.754	±.032	23.47
39 minus 12	−45.421	±.036	23.58
39 minus 4	−36.766	±.049	22.40

The reduction of these observations by the method of least squares may be conveniently carried out by the use of the form shown in table 3.

[2] George K. Burgess, *Precision machines and instruments for the measurement of length*, Proc. World Eng. Cong., Tokyo, 5, 6 (1929); paper 335.

TABLE 3.—*Calculation of corrections to meter bars at 0° C*

[1928 series of comparisons]

Observational values of (A−B) are taken from table 2.
Calculated ("most probable") values of (A−B), given in parentheses, are obtained by taking differences of Σ/5, e. g., meter 4−meter 12=+3.038−(+11.822)=−8.784 μ and meter 21−meter 27=+11.940−(+6.873)=+5.067 μ.
Correction to meter 27=−1.47 μ at 0° C. (See table 1.)
Correction to bar=correction to meter 27+(bar−27).
Length of bar=1 m+correction.

A / B	27	21	12	4	39
	μ	μ	μ	μ	μ
27	0	+5.088 (+5.067)	+5.049 (+4.949)	−3.958 (−3.835)	−40.544 (−40.547)
21	−5.088	0	−0.113 (−0.118)	−8.862 (−8.902)	−45.638 (−45.614)
12	−5.049	+0.113	0	−8.754 (−8.784)	−45.421 (−45.496)
4	+3.958	+8.862	+8.754	0	−36.766 (−36.712)
39	+40.544	+45.638	+45.421	+36.766	0
Σ	+34.365	+59.701	+59.111	+15.192	−168.369
Σ/5	+6.873	+11.940	+11.822	+3.038	−33.674
Bar−27	0	+5.067	+4.949	−3.835	−40.547
Corr. to bar	−1.47	+3.60	+3.48	−5.31	−42.02

In 1930 an intercomparison of meter bars was made by three observers, none of whom had taken part in the 1928 measurements. This new series included the two platinum-iridium meters, 12 and 21,[1] the invar meter 39, the 42 percent nickel-steel meter 153 R, and the invar meter 354. The results of these measurements are shown in table 4.

TABLE 4.—*Calculation of corrections to meter bars at 0° C.*

[Auxiliary series of comparisons, 1930]

Observational values of (A−B) are taken from the original data sheets.
Calculated ("most probable") values of (A−B), given in parentheses, are obtained by taking differences of Σ/5, e.g. meter 39−meter 12=28.45−(+16.88)=−45.33 μ
Correction to meter 21=+3.60 μ at 0° C. (See table 3.)
Correction to bar=correction to meter 21+(bar−21).
Length of bar=1 m+correction.

A / B	21	12	39	153 R	354
21	μ 0	μ −0.09 (−.08)	μ −45.50 (−45.41)	μ +2.40 (+2.37)	μ −41.61 (−41.69)
12	+0.09	0	−45.35 (−45.33)	+2.47 (+2.45)	−41.60 (−41.61)
39	+45.50	+45.35	0	+47.76 (+47.78)	+3.62 (+3.72)
153 R	−2.40	−2.47	−47.76	0	−44.04 (−44.06)
354	+41.61	+41.60	−3.62	+44.04	0
Σ	+84.80	+84.39	−142.23	+96.67	−123.63
Σ/5	+16.96	+16.88	−28.45	+19.33	−24.73
Bar−21	0	−.08	−45.41	+2.37	−41.69
Corr. to bar	+3.60	+3.52	−41.81	+5.97	−38.09

The confirmation of the difference in length found in 1928 between meters 12 and 21 is very reassuring and a change in length of meter 39 from a correction of −42.02 μ in 1928 to −41.81 μ in 1930 was not inconsistent with the change in length in this bar ever since its first standardization.

A comparison of the BIPM and NBS corrections for the platinum-iridium meter bars is given in table 5.

TABLE 5.—*Comparison of* BIPM *and* NBS *corrections for the platinum-iridium meter bars*

Length of bar = 1 m + correction.
Orig. = BIPM values at 0° C used as basis for certificates, and values at 20° C computed from BIPM certificates.
NBS 1933 = 1928 NBS observations reduced to 0° C and to 20° C using BIPM 1933 values for coefficients of expansion and for length of meter 27. (See table 1.)

Meter bars	Correction at 0° C				Correction at 20° C			
	BIPM		NBS	NBS–BIPM	BIPM		NBS	NBS–BIPM
	Orig.	1933	1933	1933	Orig.	1933	1933	1933
	μ	μ	μ	μ	μ	μ	μ	μ
27	−1.55	−1.47	−1.47	.00	+171.9	+171.67	+171.67	.00
21	+2.45	+3.42	+3.60	+.18	+176.2	+176.56	+176.74	+.18
12 (1874)	+3.32	+3.34	+3.48	+.14	+176.4	+176.09	+176.23	+.14
4 (1874)	−5.9	−5.13	−5.31	−.18	+167.6	+167.62	+167.44	−.18

Several points should be noted in considering these data. The first scientific paper of the NBS, Recomparison of the United States Prototype Meters, by Louis A. Fischer, discussed measurements made by him at the BIPM in 1903. These comparisons with laboratory working standards at approximately 17° C indicated that the length of the United States Prototype Meter 27 at 0° C was not in accord with the values determined in 1888 and given in the original BIPM certificate. An apparent shortening of 0.4 μ was shown. Mr. Fischer pointed out the desirability of recomparing meter 27 with the International Prototype Meter and with other national prototypes, and suggested the desirability of redetermining the coefficient of thermal expansion. It was decided at the NBS to continue to use the original certified value of meter 27 until further comparisons had been made. That has been done.

The measurements recently completed at the BIPM showed that a redetermination of the coefficients was indeed necessary, and that laboratory standards in use there had changed in length so that when meter 27 was compared in 1903 and meter 4 in 1907, erroneous values were reported. As comparisons were usually made at temperatures between 15 and 20° C and values were certified at 0° C, the situation is somewhat complicated. Changes in values for the corrections do not in such cases necessarily indicate changes in the physical lengths of the standards. But the change in the correction for meter 21, which has probably had more laboratory use than any other platinum-iridium standard distributed by the BIPM, is probably in large part an actual change in length. On the other hand it seems that meter 27 has not changed in length. Although the BIPM 1933 values for meters 12 and 4 are merely revisions of the results of comparisons of 1888 and 1907, respectively, the values found by the NBS indicate that the actual physical length of each of these standards may have changed, meter 12 lengthening by 0.1μ and meter 4 shortening by 0.2μ.

The adoption and use by the NBS of the new certificate for meter 27 is obviously the correct procedure. In the case of the other three platinum-iridium meters, however, it has been decided to use the results of the NBS intercomparisons. Actually the differences

between the BIPM and the NBS values are negligible as compared with the accuracy of length comparisons generally certified by a national laboratory.

2. CALIBRATION OF METER 39 TO DECIMETERS

Three calibrations of invar meter 39 have been made in recent years to determine the correction to the decimeter intervals. These measurements were made on the same longitudinal comparator as was used for the total lengths of the meter bars, using the method described in Bureau of Standards Circular 329, Calibration of a Divided Scale, by Lewis V. Judson. The results are given in table 6.

TABLE 6.—*Calibrations of meter 39 to decimeters*

Elements of calibration=corrections to intervals assuming that the total length of meter 39 is correct. Values given in columns 2, 3, and 4, are the measured values obtained in 1928, 1931, and 1932, respectively. Relative length of interval=nominal length+element of calibration.

1	2	3	4
Interval	Elements of calibration		
Decimeters:	μ	μ	μ
0 to 1	−7.20	−7.38	−7.38
0 to 2	−1.41	−1.48	−1.52
0 to 3	+1.02	+.95	+1.06
0 to 4	+2.29	+2.25	+2.30
0 to 5	−1.59	−1.56	−1.54
0 to 6	+2.27	+2.25	+2.25
0 to 7	+.05	−.02	+.02
0 to 8	−5.75	−5.85	−5.84
0 to 9	+.97	+.95	+.86
0 to 10	.00	.00	.00

III. CALIBRATION OF THE DECIMETER BARS

The calibration of the decimeter bars was carried out in two steps: first, the determination of the total lengths, and second, the calibration of the subintervals.

1. DETERMINATION OF TOTAL LENGTH

Two series of measurements were made in the determination of the total lengths of the decimeter bars. The first series consisted of an intercomparison of the seven decimeter bars among themselves, each bar being compared with each of the others. These measurements were all made on the same longitudinal comparator as was used in the intercomparison of the meters. The mean temperature was 23.65° C, and values were reduced to this temperature, using the new values given by the BIPM for the coefficients. No significant change would have been made, however, if the values originally certified had been used. These results are given in tables 7 and 8.

TABLE 7.—*Comparison of total lengths of decimeter bars at 23.65° C.*

Differences reduced to the mean temperature 23.65° C using values of coefficient of expansion given in column 10 of table 1.
A−B=Δ*L*.

Bars compared	Observed difference Δ*L*	Probable error	Observed temperature, *T*
A B	μ	μ	°C
20 minus 10	−6.26	±0.041	23.87
24 minus 10	+11.19	±.035	24.04
43 minus 10	−5.62	±.052	23.86
56 minus 10	−.99	±.021	23.90
57 minus 10	+8.04	±.042	23.98
61 minus 10	+20.79	±.033	23.26
24 minus 20	+17.28	±.044	24.00
43 minus 20	+.56	±.043	24.12
56 minus 20	+5.29	±.026	23.78
57 minus 20	+14.17	±.047	24.02
61 minus 20	+27.40	±.044	23.52
43 minus 24	−16.90	±.037	23.58
56 minus 24	−11.93	±.027	23.60
57 minus 24	−2.99	±.024	23.56
61 minus 24	+10.18	±.033	23.48
56 minus 43	+4.70	±.046	23.54
57 minus 43	+13.87	±.030	23.85
61 minus 43	+26.64	±.028	23.52
57 minus 56	+8.79	±.043	23.84
61 minus 56	+22.20	±.031	23.57
61 minus 57	+13.05	±.025	22.68

TABLE 8.—*Calculation of the most probable values of the differences in the total lengths of the decimeter bars at 23.65° C (first series)*

Observational values of (A−B) are taken from table 7.
Calculated ("most probable") values of (A−B), given in parentheses, are obtained by taking differences of Σ/7, e. g., decimeter 20−decimeter 10=−10.14−(−3.88)=−6.26μ.

A / B	10	20	24	43	56	57	61
	μ	μ	μ	μ	μ	μ	μ
10	0	−6.26 (−6.26)	+11.19 (+11.04)	−5.62 (−5.72)	−0.99 (−.97)	+8.04 (+8.00)	+20.79 (+21.06)
20	+6.26	0	+17.28 (+17.30)	+.56 (+.54)	+5.29 (+5.29)	+14.17 (+14.26)	+27.40 (+27.32)
24	−11.19	−17.28	0	−16.90 (−16.76)	−11.93 (−12.01)	−2.99 (−3.04)	+10.18 (+10.02)
43	+5.62	−.56	+16.90	0	+4.70 (+4.75)	+13.87 (+13.72)	+26.64 (+26.78)
56	+.99	−5.29	+11.93	−4.70	0	+8.79 (+8.97)	+22.20 (+22.03)
57	−8.04	−14.17	+2.99	−13.87	−8.79	0	+13.05 (+13.06)
61	−20.79	−27.40	−10.18	−26.64	−22.20	−13.05	0
Σ	−27.15	−70.96	+50.11	−67.17	−33.92	+28.83	+120.26
Σ/7	−3.88	−10.14	+7.16	−9.60	−4.85	+4.12	+17.18

The second series consisted of direct comparisons of each of the four decimeter bars belonging to the NBS with two intervals, 20 to 30 centimeters and 70 to 80 centimeters on invar meter 39. From these direct comparisons with meter 39, results were obtained as shown in column 2 of table 9.

TABLE 9.—*Total length of decimeter bars*

Length of bar=1 dm+correction

Decimeter number	Corrections at 23.65° C	
	NBS direct comparisons	NBS adjusted values
1	2	3
	μ	μ
10	-------	+5.16
20	-------	−1.10
24	+16.32	+16.20
43	−.67	−.56
56	-------	+4.19
57	+12.89	+13.16
61	+26.49	+26.23

By combining the data in table 8 with the values in column 2 of table 9, adjusted corrections at 23.65° C were obtained for each of the bars. These values are given in table 9, column 3.

Table 10 shows the NBS observations reduced to 0° C and to 20° C, using the old certified values for the coefficients, and also the new values. The original certified corrections are also shown for comparison.

TABLE 10.—*Comparison of* BIPM *and* NBS *corrections for the decimeter bars*

Length of bar=1 dm+correction. For values of coefficients see table 1

Decimeter number	Corrections at 0° C			Corrections at 20° C		
	BIPM (certificate)	NBS		BIPM (certificate)	NBS	
		Using old coefficients	Using new coefficients		Using old coefficients	Using new coefficients
	μ	μ	μ	μ	μ	μ
10	+2.0	+2.89	+2.73	+3.9	+4.81	+4.80
20	−4.5	−3.37	−3.53	−2.6	−1.45	−1.46
24	−1.8	−3.24	−3.23	+14.7	+13.22	+13.22
43	−4.0	−2.83	−2.99	−2.1	−.91	−.92
56	+.4	+1.92	+1.76	+2.3	+3.84	+3.83
57	−6.0	−6.28	−6.27	+10.5	+10.18	+10.18
61	−3.2	−3.79	−3.78	+22.1	+21.54	+21.53

2. CALIBRATION OF THE SUBINTERVALS

The calibration of subintervals was made for the same intervals as was done for the original BIPM certificates, namely, for the centimeter intervals, for the millimeters of the first centimeter and for the tenth-millimeters of the specially graduated millimeter.

Most of the measurements were made on the longitudinal comparator, although some of the work at the beginning was done on a linear dividing engine used as a comparator.

The general scheme used in the original calibration at the International Bureau was carried out. Guillaume's method[3] for the reduction of the observations was employed as in the work done at Sèvres.

A good idea of the results of the calibration will be obtained by considering the calibrations of decimeter 43, expressing the results as "element of calibration", that is, the corrections which the subintervals have if the length of the whole interval is considered as correct, as will be clear from a consideration of table 11.

TABLE 11.—*Elements of calibration of decimeter 43*

Elements of Calibration=corrections to intervals assuming that the total length (100, 10, or 1.0 mm) is correct.
Relative length of interval=nominal length+element of calibration.

Interval	BIPM	NBS values using auxiliary decimeter indicated						
		Dm 10	Dm 20	Dm 24	Dm 56	Dm 57	Dm 61	Mean
Millimeters:	μ	μ	μ	μ	μ	μ	μ	μ
0 to 10	+1.0	+0.92	+0.91	+0.96	+1.04	+0.82	+1.11	+0.96
0 to 20	+1.1	+.95	+.95	+.84	+1.00	+.72	+.98	+.91
0 to 30	+.6	+.55	+.46	+.42	+.58	+.30	+.61	+.49
0 to 40	+.3	+.05	+.24	.00	+.21	−.12	+.05	+.07
0 to 50	+.6	+.39	+.67	+.35	+.53	+.13	+.41	+.41
0 to 60	+.7	+.37	+.62	+.33	+.55	+.26	+.43	+.43
0 to 70	−.1	−.39	.00	−.34	−.13	−.48	−.41	−.29
0 to 80	−1.4	−1.67	−1.33	−1.75	−1.41	−1.81	−1.66	−1.60
0 to 90	−1.0	−1.22	−.83	−1.18	−.89	−1.07	−1.06	−1.04
0 to 100	.0	.00	.00	.00	.00	.00	.00	.00
0 to 1	−.2	−.06	−.02	−.10	−.15	−.05	−.06	−.07
0 to 2	+.1	+.10	+.22	+.15	+.14	+.14	+.16	+.15
0 to 3	−.1	.00	+.02	+.04	+.07	+.05	+.09	+.04
0 to 4	+.1	+.01	+.15	+.08	+.12	+.10	+.20	+.11
0 to 5	−.1	−.11	−.03	−.07	−.07	−.13	+.01	−.07
0 to 6	−.1	+.04	+.01	−.07	−.04	−.10	+.04	−.02
0 to 7	+.5	+.30	+.39	+.32	+.41	+.38	+.49	+.38
0 to 8	+.4	+.42	+.43	+.42	+.42	+.30	+.41	+.40
0 to 9	+.3	+.24	+.26	+.28	+.24	+.19	+.32	+.26
0 to 10	.0	.00	.00	.00	.00	.00	.00	.00
0 to 0.1	.0	−.10	−.10	+.06	−.07	+.21	+.10	+.02
0 to 0.2	−.2	−.18	−.21	−.16	−.15	−.17	+.10	−.13
0 to 0.3	−.4	−.27	−.89	−.09	−.71	−.01	+.02	−.32
0 to 0.4	−.9	−.62	−.82	−.55	−.81	−.72	−.66	−.70
0 to 0.5	−.8	−.66	−.79	−.70	−.80	−.75	−.57	−.71
0 to 0.6	−1.2	−1.04	−1.14	−1.11	−1.20	−1.22	−1.07	−1.13
0 to 0.7	−1.2	−.96	−1.16	−1.06	−1.09	−1.24	−1.04	−1.09
0 to 0.8	−.9	−.64	−.90	−.80	−.84	−.75	−.79	−.79
0 to 0.9	−.4	−.17	−.18	−.36	−.25	−.38	−.20	−.26
0 to 1.0	.0	.00	.00	.00	.00	.00	.00	.00

The interval is given in the first column, the element of calibration as obtained in the BIPM calibrations in the second column, the several elements of all calibrations as obtained at the NBS by comparison with each of six decimeters, and the mean of these six values in the following columns.

Although there are variations between the several sets of values, these are not excessive when the conditions of the lines and surfaces of these decimeter bars are taken into consideration. They are discussed further in the next section. The mean value of the element of calibration is certainly sufficiently accurate for our purposes.

The lengths of the subdivided millimeters were determined from known millimeter intervals on these decimeter bars. The results, compared with the original values, appear in table 12.

[3] C. E. Guillaume, *L'étalonnage des échelles divisées*. Travaux et Mémoires du Bureau International des Poids et Mesures, **13**, 1–54 (1907).

TABLE 12.—*Corrections to subdivided millimeters of decimeter bars*

Length of interval=1 mm+correction

Decimeter number	Correction at 0°C	
	BIPM certificate	NBS determinations
	μ	μ
10	----------	+0.28
20	----------	+.14
24	−0.2	+.20
43	−1.0	−.59
56	----------	−.50
57	−.1	−.21
61	−1.6	−.91

IV. SOURCES OF ERROR

The more important sources of error in all comparisons of line standards of length are these: (1) an uncertainty regarding the actual temperature of the bars as to whether or not each bar is in thermal equilibrium at the temperature indicated by the thermometer; (2) difficulties in setting upon the lines, owing to defects in the lines and in the polished surfaces on which they are ruled; and (3) personal errors in setting on the lines, resulting in differences between the results obtained by different observers. These differences are enhanced by the defects in the lines and surfaces.

Sears and Barrell of the National Physical Laboratory, Teddington, England, have recently stated:[4]

> In the authors' opinion the average accuracy of repetition generally attainable in the comparison of two line standards of the best class, such, for example, as the Prototype Metre and its National Copies, is of the order of 0.25×10^{-6} M, which corresponds to a possible range of values of about ±1 part in 8,000,000.[5] Differences of this order of magnitude are liable to occur between the results of comparison of the same bars by different observers.

From the context it is obvious that they regard the condition of the lines and surfaces as an important factor in causing such variations. All of which agrees with the experience of the NBS.

In the comparison of the meter bars the smallness of the residuals, that is, the differences between the observed and computed values of table 3, indicates that the bars were in good thermal equilibrium at the time the observations were made. The comparator is in a basement room; several hours elapsed between sets of measurements; and precautions were taken to maintain uniform temperature.

In the calibration of the decimeter bars the effect of temperature is very small. It will be noted that in the case of the invar bars, an error of 0.1° C in the temperature measurement would result in an error in the length of one of these bars of only 0.01μ. Even in the case of the nickel bar, 0.1° C corresponds to 0.1μ. Special care was used to insure that the bars and thermometers had come to a condition of equilibrium. It is not likely, therefore, that there are in this work any errors of significance ascribable to variations in temperature, or to errors in temperature measurement. A comparison of tables 3 and 4, representing measurements by different observers,

[4] J. E. Sears, Jr., and H. Barrell, *Determinations of the fundamental standards of length in terms of the wavelength of light*, Phil. Trans. Roy. Soc. London, **233**, 173 (1934).

[5] This apparently should be ± 1 part in 2,000,000.

with three bars in common, indicates that these measurements of the meter bars are free from any large personal errors.

The probable error of each of the values of the elements of calibrations of meter 39 in table 6 is approximately 0.03μ.

That there are relatively large errors in our work with the decimeter bars is readily explained by the imperfections of the lines and surfaces. The probable error of each of the calculated differences in total length of the seven bars, as determined by their direct intercomparisons (table 8), is $\pm$ 0.05μ. By excluding the nickel bar 61 because the residuals on this bar are seen to be large, a probable error of $\pm$ 0.04μ is obtained for the other six. Using the four invar bars, "best values" for the differences in length are obtained differing a few hundredths of a micron from those listed above but the probable error is only 0.02μ. However, consideration of the character of the lines and of the surfaces on which they were ruled has led us to the conclusion that measurements of the total length of these bars to better than about 0.05μ are without real meaning. The entire series of measurements with all seven bars has therefore been retained, and the relative results of the intercomparisons at 23.65° C are considered correct to about 0.1μ.

The chief source of error in the final value for the total lengths of the decimeter bars (columns 3, 4, 6, and 7 of table 10) is in the determination of the absolute values of the four decimeter bars, 24, 43, 57, and 61, belonging to the NBS, but careful study of the results leads to the conclusion that the final correction to the total lengths of each of the seven bars is not in error by more than 0.2μ, and that in most cases it is not in error by more than 0.1μ.

To what extent the differences between the old and the new values represent changes in the actual length of the bars, and to what extent they represent a greater accuracy in the newer measurements, it is hardly possible to state. Undoubtedly some of the changes are real changes in the length of the bars. As the measurements at the NBS were made with precise comparators of modern design, with high-power microscopes, and under such conditions as to yield accurate results, it is believed that the NBS is justified in adopting these new determinations as representing the true values at the time of measurement more nearly than could any value given by a certificate based upon measurements made one or more decades earlier.

In the calibration of the subintervals of the decimeter bars (see table 11 for decimeter 43), there are variations amounting to as much as 0.5μ. That these are caused by imperfections in the lines and surfaces of the decimeter bars, and not by the comparator, is demonstrated, not only by the measurements on the meter bars, but more especially by several sets of comparisons on decimeter scales ruled by C. G. Peters of the interferometry section on highly polished and almost flawless surfaces of bars of stainless steel. Those lines were very sharp and straight and had even edges, and with those scales measurements consistent to about 0.05μ were made. Therefore, with improvements in the surfaces and lines of line standards and commercial scales, this comparator is capable of a corresponding reduction in the uncertainty in the measurements.

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V. CONCLUSION

From the extensive calibrations reported in this paper, the National Bureau of Standards is enabled to adopt precise values for the corrections for its meter and decimeter bars. These values are all based on the values assigned to the United States Prototype Meter 27 by the Bureau International des Poids et Mesures, and on the latest and most precise values for the coefficients of thermal expansion of the several bars.

The authors acknowledge the whole-hearted cooperation of Merriel M. Gardner, V. H. Knoop, and other members of the length section, who have rendered constant assistance in the extensive measurements and computations involved.

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ULTRAVIOLET TRANSMISSION CHANGES IN GLASS AS A FUNCTION OF THE WAVE LENGTH OF THE RADIATION STIMULUS

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ABSTRACT

Continuing the research previously reported in Research Paper 113 further consideration is given to methods of testing the photochemical stability of window glass made for transmitting short wave length ultraviolet solar radiation. It is shown that accelerating the stabilization of the transmission of window glass (equivalent to the stabilization produced by sunlight) by means of filtered ultraviolet radiation from the quartz mercury arc is impracticable principally because of the antagonistic action of radiation of wave lengths in the region of about 365 mμ which reverses, in varying degrees, the photochemical reaction produced by the shorter wave lengths.

A new phenomenon in the ultraviolet transmission behavior of certain glass is reported. The phenomenon may be briefly described as follows: When irradiated with light of a given wave length (in the region 250 to 365 mμ) the sample of glass reaches an equilibrium state in which the transmission (at 302 mμ, for example,) attains a certain value, which is a constant for the given wave length stimulus. The equilibrium value of the transmission is different for each wave length of the radiation stimulus, increases with increasing wave length of the stimulus, and is independent of the previous order of treatment of the glass.

In place of a chemical analysis, the absorption spectrum (which is a characteristic of every chemical compound), is used as a criterion for judging the magnitude of photochemical action produced by ultraviolet radiation of different wave lengths of homogeneous radiation.

In the soda-lime-silica glasses examined (whether or not they contained an appreciable amount of iron oxide) the photochemical equilibrium was found to be different for each wave length of homogeneous radiation to which the glass reacts. To attain this equilibrium the reaction, caused by a given wave length, is in the direction to either increase or decrease the transmission, depending upon the existing condition developed by previous heat treatment or by previous exposure to other wave lengths to which the glass reacts.

Using homogeneous radiation, no wave length (at least not for wave lengths shorter than and including 365 mμ) was found that has the exclusive property of either increasing or decreasing the ultraviolet transmission in the soda-lime-silica glasses examined.

The longest wave length having an appreciable photochemical action on a soda-lime-silica glass is at about 405 mμ. For wave lengths 365 mμ and shorter, the photochemical action as determined by the equilibrium levels in spectral absorption, is a function of the wave length (the frequency) of the radiation stimulus; the shorter the wave length the greater the photochemical action in the direction of greater absorption.

In contrast with a soda-lime-silica glass, a phosphate-lime glass (containing oxides of Al, B, Na, Mg, Si, and Fe as minor constituents) is depreciated in ultraviolet transmission only by wave lengths shorter than about 290 mμ. After depreciation, the ultraviolet spectral transmission curve of the calcium phosphate glass is similar to that of a soda-lime-silica glass. Nevertheless, exposure of the depreciated calcium-phosphate glass to homogeneous radiation of wave lengths 297 to 365 mμ does not appreciate the transmission, as is the case in the soda-lime-silica glass. In other words, in contrast with the soda-lime-silica glass, certain wave lengths have the property of decreasing the ultraviolet transmission; but in the spectral range investigated no reverse reaction was observed.

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I. INTRODUCTION

The object of the present paper is twofold: (a) to describe the results of studies of the depreciation and appreciation (the so-called "solarization and rejuvenation") of the ultraviolet transmission of window glasses, by exposure to filtered and unfiltered heterogeneous radiation from the sun, and from the quartz mercury arc, and (b) to describe some preliminary results of similar studies of photochemical changes in glass produced by isolated wave lengths of homogeneous radiation from the quartz mercury arc.

The information derived from the first study (a) is of commercial importance in connection with methods of testing the photochemical stability, by accelerating the aging of special window glass made for transmitting short wave length ultraviolet solar radiation shut out by common window glass.

The information derived from the second study (b), which has resulted in the discovery of a new phenomenon in the ultraviolet transmission behavior of certain glasses, is of importance in connection with the question of the "antagonistic" action of different wave lengths in photochemical reactions, and may perhaps contribute to the elucidation of claims of antagonistic action of different wave lengths in certain biological reactions, particularly supposed changes in the constituents of the blood (hemoglobin).

Although the literature contains numerous papers (9) [1] on the so-called "antagonistic photochemical and photographic effects of different wave lengths of thermal radiation", but little information seems available on the reversibility (2) (3) of a photochemical reaction that occurs in certain window glasses (incidentally containing a small amount of iron oxide as an impurity) when exposed to heterogeneous radiation of different wave lengths. In fact, the herein described experiments appear to disclose an entirely new phenomenon, namely, the reversibility of a photochemical reaction in glass, the direction of the reaction caused by a single wave length of homogeneous radia-

[1] Figures in parentheses here and throughout the text and footnotes indicate references and notes given at the end of this paper.

tion depending upon the existing chemical condition developed in the glass as a result of previous exposure to radiation of other wave lengths. Whether this phenomenon is a result of the occurrence of more than one photochemical reaction remains undetermined (16).

It has been known for more than two decades that ferrous oxide in glass is more transparent to ultraviolet radiation than ferric oxide; and this observation is now the basis for making glasses to protect the eyes from injurious ultraviolet radiation by keeping the iron oxide in the ferric condition.

On the other hand, because of the low transparency of ferric oxide in the ultraviolet, the problem in the manufacture of special window glasses for transmitting short wave length ultraviolet solar radiation shut out by common window glass, is to procure raw materials that are as free as possible from iron.

Recently Starkie and Turner (13) made a quantitative investigation of soda-lime-silica glasses prepared from carefully selected materials containing a negligible amount of iron oxide. Small amounts of pure ferric oxide were progressively added to form a series of glasses containing from 0.005 to 1.0 percent (calculated) of iron oxide. Of the total iron in each sample 93 percent was in the ferric condition; and, in agreement with their expectations, these glasses (while being lower in initial transmission) did not depreciate in transmission on exposure to ultraviolet radiation.

On the other hand, in certain commercial glasses in which 31 to 48 percent of the total iron oxide present was in the ferrous condition before irradiation, the ultraviolet transmission decreased coincidently with the reconversion of ferrous into ferric oxide by irradiation, the ferrous oxide falling to about 20 percent of the total. At this stage the transmission had become relatively stable to the total ultraviolet radiation from the carbon arc lamp.

Starkie and Turner (13) cite experiments by Sugie (21) showing that in a soda-lime-silica glass the ferric oxide lowered the ultraviolet transmission more than the ferrous oxide; whereas in a potash-lime-silica glass there was no difference between the two forms (23).

It has been found recently (2) (3) that the stability of the transmission of the glass is a relative term, depending upon the wave length of the activating radiation.

The present research shows the readiness with which the photochemical reaction in a soda-lime-silica glass made from pure materials (also samples containing iron oxide as an impurity, and, in some cases, containing oxides of As or Mn as a decolorizer) is reversed by merely changing the wave length of the exciting radiation. It shows also the facility with which the reversibility of this reaction can be studied qualitatively by physical methods (that is, by spectral ultraviolet radiometry) even though we cannot, as yet, correlate the physical measurements with the photochemical products formed in the glass, as would be deduced by chemical analysis.

In previous reports (10), (11), data were given on the rejuvenation in transmission of glasses by heat treatment. But this, insofar as is known and, in contrast with the herein-described photochemical reaction (which appears to be an unusual phenomenon that deserves further investigation) is not in the same sense a reversible process. For this suggested investigation a glass should be used that is made of materials that are relatively nonphotosensitive in the spectral region

under investigation; and also other glasses by using in addition varied amounts of supposedly photosensitive materials (e. g., oxides of sodium, arsenic, iron, manganese, phosphorus, etc., and also combinations of these materials). From an investigation of such glasses it should be possible to elucidate the herein-described equilibrium levels of photochemical stability for different wave lengths and for different materials.

From the foregoing citations it is to be noted that, heretofore, the transparency and photochemical stability of a window glass (a soda-lime-silica glass) has been discussed with reference to the iron oxides present as an impurity, the ferrous oxide being assumedly changed into the ferric by the action of the ultraviolet rays. But no attempt seems to have been made to determine: (a) whether the photochemical instability is in the pure soda-lime-silica glass, or is a result of the presence of the iron oxides; (b) whether the oxide of iron changes from the ferrous to the ferric condition because of the oxygen set free in the main constituents; (c) whether the iron oxides act as catalyzers in increasing the photochemical reaction in the soda-lime-silica constituents; or (d) whether the photochemical reaction in the relatively iron-free soda-lime-silica glass is a result of the presence of dissolved CO_2 or H_2O. The latter has a catalytic action in photolysis (20).

From the herein-described experiments on various special window glasses (10), some having a lower iron oxide content than others, and on a sample of soda-lime-silica glass, prepared from pure materials,[2] it appears that a soda-lime-silica glass, practically free from iron, is photosensitive.

The present investigation is, therefore, being undertaken anew, using pure (iron-free) materials to determine the photochemical stability of oxides of Na, Ca, K, As, etc., in various glasses which, for purposes of comparison, are being prepared by different methods in different laboratories (23).

This Bureau's interest in the question of the solarization of special window glasses, marketed for transmitting short wave length (290 to 310 mμ) solar radiation shut out by common window glass, began in the spring of 1927, and in the following October a report was issued (1) stating that all these new window glasses decrease in transparency when exposed to the sun, to the carbon arc, and to the quartz mercury arc; and that the stabilized transmission depends in some undetermined manner upon the (ferrous and ferric) iron oxides present as an impurity.

It was found also, on exposure of the glass to the unfiltered radiation from a quartz mercury arc lamp (which emits radiation of wave lengths shorter than 290 mμ; not present in sunlight), that the ultraviolet transmission was reduced to a lower value than that obtained by exposure to the sun.

Subsequently it was found by Wood and Leathwood (2) and also by the writers (3) that exposure of the glass to sunlight, after exposure to the mercury arc lamp, restores the ultraviolet transmission close to the minimum value obtained by exposure only to the summer sun, thus explaining an earlier discrepancy in transmission measurements of the Bureau and the Smethwick, England, laboratories on a sample of irradiated glass that during the interchange between

[2] Supplied by F. C. Flint of the Hazel Atlas Glass Co., in December 1928. Recently samples of pure (relatively iron-free) soda-lime-silica and soda-silica glasses, prepared by A. N. Finn of this Bureau, were found to be unstable photochemically.

the two laboratories had undergone partial rejuvenation by exposure to daylight.

Moreover, when the exposure was made to the sun in the winter, i. e., when the wave lengths shorter than 305 mμ were almost entirely absent, it was found by the writers that there was an apparent overshooting of the recovery in transmission (3) (4) which was not permanent. With the advancing spring season the transmission decreased again to a value that is closely the same as that attained by exposure only to the summer sun. As shown in the present paper, this was probably owing to the fact that the short wave length ultraviolet (less than 305 mμ), absent in winter sunlight, counteracts the rejuvenating action of the ultraviolet rays of wave lengths in the region of 365 mμ.[3]

In order to demonstrate that this rejuvenation in transmission is selective as to wave length, samples of glass were first exposed to the unfiltered radiation from the quartz mercury-arc lamp (3) and then exposed to the same lamp through suitable glass filters. In the same manner duplicate samples were solarized by exposure to unfiltered sunlight and then reexposed to sunlight filtered through suitable screens (4) (5), as more fully described in the present paper.

This solarization and rejuvenation was carried through several cycles (5) (6), using solar radiation and quartz mercury arc radiation as sources. In both cases the results were conclusive in demonstrating that the wave lengths in the spectral range of 313 mμ to 405 mμ have the power of reversing the photochemical action produced by the shorter wave lengths.

Since the mercury arc spectrum is highly discontinuous, with but few emission lines in the region of 297 to 365 mμ, it is impossible to provide a filter for mercury arc solarization tests that will produce a spectral energy distribution similar to sunlight, although the photochemical action of such filtered radiation may perhaps be approximately the same as sunlight. Stockbarger's (8) data seem to show a similarity in the effect of sunlight and a filtered mercury-arc radiation. It will be noted, however, that his exposures to the sun were made during the months of January to March when, as will be shown presently, the solarization is not as effective as in summer sunlight. Consequently, as previously noted by the writers (6) (7), the stabilized transmission obtained by exposure of the glass to filtered radiation from the mercury arc may not be as low (depending upon the filter) as that obtained by exposure to direct summer sunlight, and hence the use of filtered radiation from the quartz mercury arc may be less reliable than unfiltered radiation in making stabilized transmission tests. Another objection to stabilizing the glass under a filter is the long exposures required.

The method of correlating the stabilized transmissions obtained on exposure to the mercury arc and sunlight, respectively, was given in a previous communication (3) in which it is shown that the great variations in transmission of different melts of the same kind of glass outweight the relatively small uncertainties in the accelerated stabilization of the transmission by using the unfiltered mercury-arc radiation. Moreover, the requirement of long exposures (some 200 hours) to filtered radiation (7) and of new filters for each new acceleration test (6) makes the filter method less practicable than the stabilization of

[3] While this is an interesting scientific observation, as already indicated (5), the actual amount of recovery in transmission of an ultraviolet window glass, during the winter, is not sufficient to warrant recognition in the sales promotion of window glasses that solarize on exposure to (summer) sunlight.

the transmission by means of unfiltered radiation and adjustment of the value by a factor based on average values obtained from previous observations on samples of the same make of glass, stabilized by exposure to the lamp and to the sun (3).

II. EXPERIMENTAL PROCEDURE

In a previous paper (10) it was shown that whenever there is a change in the ultraviolet transmission of glass, either as the result of solarization by exposure to heterogeneous ultraviolet radiation, or of rejuvenation by heat treatment, this change is not confined to a narrow band of wave lengths, but extends from about 405 mμ to an undetermined wave length shorter than 254 mμ. On a subsequent page it is shown that this same phenomenon occurs when the solarization and rejuvenation are produced by homogeneous radiation. That is to say, whatever the new substance (or substances) may be that is formed by photochemical action, its absorption spectrum is not confined to narrow bands (as for example, obtains in irradiated ergosterol) but extends over a wide region into the shortest ultraviolet (to an undetermined wave length) where it is submerged by the exceedingly high absorption of the main constituents of the glass.

Hence, in view of the impracticability of determining the complete spectral ultraviolet transmission curve after each irradiation of the glass, in the present as in the previous investigation (10), the transmission for the emission line of the quartz mercury arc, at the wave length 302 mμ, is used as an indicator of the photochemical change produced in the glass by irradiation.

For this purpose a spectroradiometer, consisting of two uncemented quartz-fluorite achromatic lenses, 33 mm in diameter and 30 cm focal length, and a quartz prism 6 cm in height, was used (15). This produced a long spectrum from which the emission line at 302 mμ was easily isolated and the transmission of the glass, for this line, was measured by means of a previously described vacuum thermopile and ironclad Thomson galvanometer.

The source of ultraviolet for these transmission measurements was a vertical "Uviarc" quartz mercury-arc lamp, focused upon the spectrometer slit by means of an achromatic lens of quartz-fluorite. Since even a short exposure of these highly photosensitive glasses to the unfiltered radiation from this lamp produced an appreciable decrease in their transmission (if above the equilibrium level for the total radiation of the lamp), a plate of Corex-D glass (having a transmission of 50 percent at 302 mμ and less than 1 percent at 280 mμ) was mounted in front of the arc, during the transmission measurements, at 302 mμ and longer wave lengths. As a further precaution, in most cases when the transmission was above 25 percent at 302 mμ, a glass filter (having a transmission of 5 percent at this wave length) was used, and the value at 302 mμ calculated from the observed transmission at 313 mμ. When the transmission was below 20 percent (at 302 mμ) no filter was used.

For investigating the photochemical action of homogeneous radiation, the above-mentioned vertical quartz mercury arc lamp was operated at a constant potential (70 volts). The single wave lengths were isolated by means of a high-powered quartz spectropyrheliometer, as used in previous investigations (14). The intensities of the lines at the exit slit were evaluated in absolute units.

The sample to be irradiated with homogeneous radiation was securely attached to a suitable support which could be mounted in a fixed position directly back of this exit slit for irradiation purposes; and in a fixed position before the entrance slit of the quartz-fluorite spectrometer for transmission measurements. Since the width of the irradiated part of the sample was about 1 mm, and the transmission measurements were made upon the central portion of this irradiated area, about 0.5 mm in width, there is practically no uncertainty in making the transmission measurements upon the central part of the irradiated area.

Most of the measurements using heterogeneous filtered radiation preceded the work with homogeneous radiation. In the preliminary search (3) (4) for the approximate wave-lengths of the exciting radiation (effective in producing solarization and rejuvenation of the

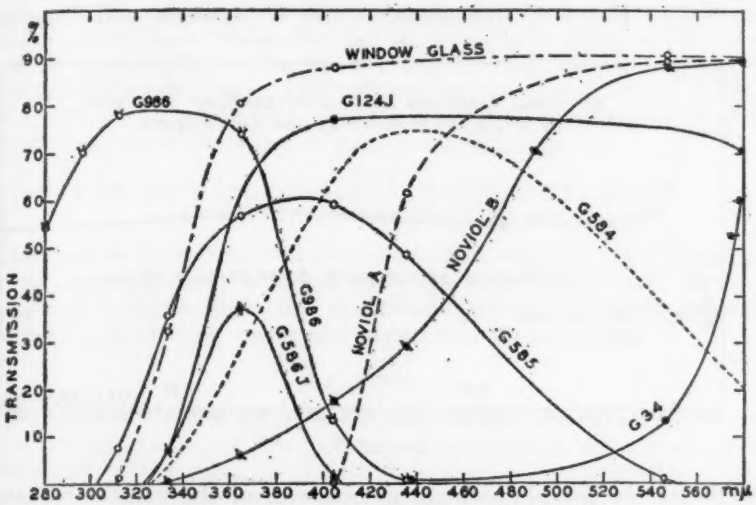

FIGURE 1.—*Spectral transmission of filters used.*

transmission of glasses), a series of nine filters, including red, yellow (Corning G34 and Noviol B), green (G584 and 585), violet (G586J and G986), and colorless window glass, was used to isolate wide spectral bands of solar and quartz mercury arc radiation. The spectral transmission curves of these filters are depicted in figure 1.

Additional samples of the glasses under investigation were wrapped in black paper, used in protecting photographic plates, and exposed to the source to determine the effect, if any, of heating (to 40 or 50° C) as distinguished from the rejuvenation by heat treatment, which requires a temperature of 200° C or higher (10) (11) to be effective.

After finding that the maximum rejuvenation is caused by wave lengths in the region of 340 mμ to 405 mμ, the investigation was continued with fewer filters and, for convenience, principally glass G584.

The samples of glass exposed under the filters were about 5 cm long, 1 cm wide, and 2.6 mm thick. The edges of the samples were painted with asphaltum varnish in order to prevent scattered radiation from entering the glass through the edge after passing around the filter. In this manner only radiation that had passed through the filter could enter the glass.

While nearly all of the various makes of special window glasses were found to decrease in ultraviolet transmission on exposure to the sun, and to artificial sources of ultraviolet radiation (10), (and could be rejuvenated by the herein described methods), most of our observations were made on a sample of Vitaglass which was found to be especially photosensitive and which was available in a suitable thickness (about 2.6 mm) and in a sufficient quantity at the time this investigation was undertaken.

III. EXPERIMENTAL DATA

Under this caption are given various data on solarization and rejuvenation of special window glasses that are transparent to short wave-length ultraviolet radiation. In the preliminary tests a phosphate glass (Corex A) and the following silicate glasses were under observation: Brephos, Helioglass, Sunlit, Uviol-Jena, and Vitaglass.

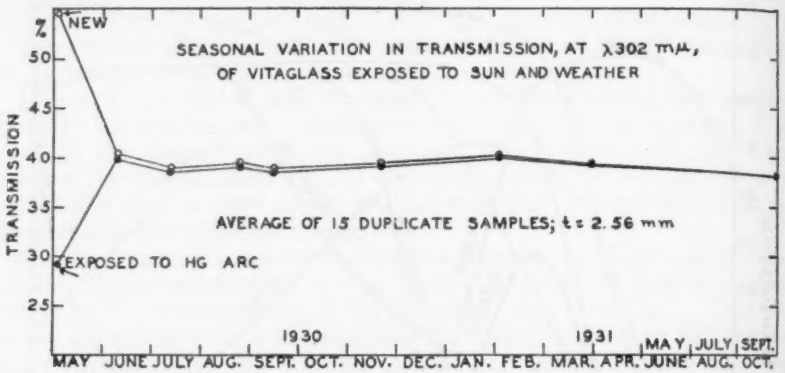

FIGURE 2.

Qualitatively the photochemical behavior of the various makes of silicate window glasses was found the same. Hence to simplify the presentation, a description is given of our observations only on Vitaglass, which has been on the market the longest and has thus afforded an opportunity for the most complete photochemical study.

1. SEASONAL VARIATION IN TRANSMISSION OF SPECIAL WINDOW GLASSES

Supplementing the earlier observations on various makes of glass (4) (5) in figure 2 is shown the seasonal variation in the ultraviolet transmission (at 302 mμ) of Vitaglass exposed to the sun and weather for about 2 years.

Fifteen pairs of samples of this kind of window glass (2.5 by 5 cm) were used for this test. One sample of each pair was exposed to the quartz mercury arc for 10 hours (10). After this, the 30 samples were mounted in a frame (similar to a window frame) inclined at an angle of 45 degrees, facing south on the roof of a building,[4] and exposed continuously day and night.

[4] All exposures to solar radiation reported in this paper were made at the National Bureau of Standards, Washington, D. C.

After an exposure of about 6 weeks (May 1 to June 10, 1930) the average transmissions of both sets of samples had become practically stabilized at about 40 percent, decreasing to 37 percent by September. (See fig. 2.)

During the winter months, owing to the low intensity or perhaps to the entire absence of the wave lengths shorter than about 300 mμ, there is a slight rejuvenation (amounting to about 1 percent) in transmission. However, this increase in transmission is so small that the average of a large number of samples is required to demonstrate the fact. Incidentally it is to be noted that this glass showed no appreciable surface weathering, the slight decrease in transmission during the second year no doubt being the completion of stabilization.

At the time of the writing of this paper most of the above-mentioned glasses had been exposed out of doors continuously for over 4 years, and the results show that after stabilization by exposure to the summer sun for about 3 months, the transmission remains practically constant, at a value which, for the most unstable glass, is only some 15 to 20 percent below the unstabilized transmission which obtains in the freshly made glass. This refutes rumors, circulated early in the production of these glasses, that they lose their ultraviolet transparency entirely after being in use for a short time.

2. EFFECT OF HETEROGENEOUS ULTRAVIOLET RADIATION UPON THE TRANSMISSION OF GLASS

The various data obtained relative to the effect of filtered and unfiltered heterogeneous radiation upon the ultraviolet transmission of (Vitaglass) window glass are described under three main captions ("Series"), depending upon the experimental procedure.

(a) SERIES I

In order to eliminate the additional effect of weathering, if any, during the study of the photochemical reaction as a function of the wave length of the exciting radiation, in the first experiments a group of glasses were exposed only when the sun shone and at all other times kept in the laboratory.

The exposures were made at approximately normal incidence. To accomplish this the glasses, with their ends resting on slats, were securely mounted upon (but separated from) a suitably inclined board which was placed upon a window sill and kept adjusted approximately normal to the sun's rays during the exposures.

After solarization by exposure to the total radiation from the quartz mercury arc for 10 hours, the glasses were mounted, as described above, and covered with filters of black paper, black celluloid (transparent to the infrared rays), or various glasses (either singly or in combination). The spectral transmissions of these filters are illustrated in figure 1.

In figure 3 are shown the results obtained with five samples of Vitaglass AG–2A with the filters indicated. Eight samples were actually tested under the following filters: (black paper; black celluloid; red glass; orange glass, G34; yellow Noviol B; light blue-green, G124J, plus Noviol B; purple, G986; and a deep blue-green, G584), but to avoid confusion in the illustration, the results obtained with three of the filters are not shown.

As shown in figure 3, an exposure of 140 hours to winter sunlight (from November 9, 1929 to January 14, 1930)[5] filtered through G584 increased the transmission of this sample from 18 to 29 percent. The results for the other samples during this initial period are not illustrated.

All of the samples were again exposed to the unfiltered mercury arc for 5 hours and then a new series of exposures to the sun was begun (1:14:30).

It is to be noted, as shown in figure 3, that the samples under black paper and red glass respectively increased but little in transmission. The same was true of the sample exposed under black celluloid.

The transmission of the sample under the orange-colored filter, G34 (not illustrated in fig. 3) increased in transmission from 18.5 to only 23.5 percent in 400 hours, showing that radiation in the yellow, red, and infrared had but little rejuvenating effect.

The samples under Noviol B and under Noviol B plus G124J increased from 18.5- to 25-percent transmission, but there was in these cases some uncertainty about the effect of unfiltered light getting around the filters.

At first (1:14:30 to 4:19:30) the sample that was not covered with a filter underwent the greatest rejuvenation; next, the sample that was covered with the ultraviolet transmitting glass G986; then both decreased in transmission to 25.5-percent transmission at the expiration of 590 hours exposure. On the other hand, the sample under filter G584 increased in transmission to 29.5 percent (at 6:26:30). The latter sample was then reduced in transmission (to 26.5 percent) by exposure directly to the sun for 2 days, after which a further exposure of 300 hours (9:26:30) under G584 increased the transmission to 30.4 percent.

It is of interest to note, however, that in the period 1:14:30 to 6:26:30 the sample of Vitaglass exposed under the filter G584, which is opaque to radiation of wave lengths shorter than about 330 mμ, underwent a greater recovery in transmission than a duplicate sample exposed under G986 which is transparent to wave lengths shorter than 330 mμ. As will be shown presently, these short wave lengths produce stabilization at a lower transmission level.

At this stage of the observations an exposure of 10 days to direct autumn sunshine (9:26 to 10:7:30) produced less solarization than 2 days in summer (6:26:30).

These samples were then placed upon a deep ledge facing south (shielded from the rain) and exposed continuously, under the filters, without adjustment for normal incidence to the sun. During the winter months the transmission of the sample under the filter G584 did not increase above 29.2 percent, and direct exposure to the sun (no filters) for 10 days (1:20 to 1:30:31) produced but little solarization, indicating a close balance in the so called "antagonistic" action of the ultraviolet, when radiation of wave lengths 290 to 305 mμ is very weak or entirely absent.

In this locality there is a rapid increase in the ultraviolet intensity in February (17). This is shown by the relatively rapid recovery in transmission (to 30 percent) of this sample of glass on exposure to the sun under the filter G584, for 11 days (2:11:31); and by the subsequent increase in transmission to 31.2 percent in June 1931, when this series of observations was discontinued.

[5] In the text and illustrations such specific dates are, in most cases, abbreviated thus: 11:9:29 to 1:14:30.

From the results obtained with these filters, particularly with the filters G584 and G986, it was concluded that the wave lengths most active in causing an appreciation in transmission are situated between 330 mμ and 405 mμ.

(b) SERIES II

Although in the foregoing experiments the samples that were wrapped in black paper showed little or no change in transmission as a result of warming on exposure to solar radiation, it was desirable to make further observations concerning this question.

Instead of using slats on a board to support the glasses, a thin, light-tight wooden box (length 35 cm; width 10 cm; inside depth 5 cm) was provided. The outside of this box was painted with aluminum; and the inside was painted black. Ventilation was obtained through openings in the back of the box, covered with baffles painted black, and so arranged that light could not enter the enclosure.

The top of the box (5 mm in thickness) contained holes over which were placed the filters on the outside, and the samples of Vitaglass on

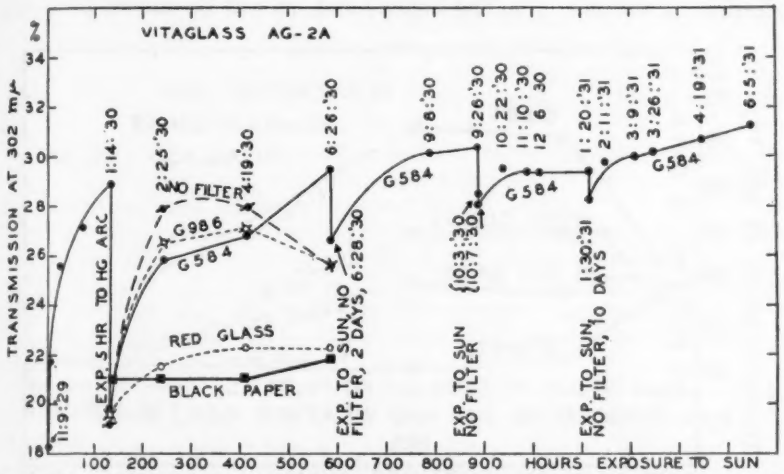

FIGURE 3.—*Variation in spectral transmission of a sample of Vitaglass, using filtered and unfiltered solar radiation.*

Exposures for first 900 hours made only when sun shone.

the inside. One sample, wrapped in black paper, was placed in the box near the samples exposed to the sun. To shield the samples of glass from dust, rain, and moisture, the edges of the filters were attached to the top of the box by means of Chatterton wax.

The filters used in this experiment were Corning glass G584, a piece of ordinary window glass (fig. 1), and a polished plate of crystalline quartz (7). The latter was used to shield the sample from the wind and weather, and to provide temperature conditions closely similar to the other samples, without shutting out the ultraviolet rays.

Another variation from series I was the "solarization" of the glass by the sun, instead of the quartz mercury arc lamp, before exposure under the filters.

In this rejuvenation test the box containing the samples was mounted on the roof of a building. The samples, in the box, facing

south at an angle of 45° to the vertical, were exposed continuously without adjustment to normal incidence to solar radiation.

Before beginning this series of rejuvenation tests the samples of Vitaglass under investigation were partially solarized by exposure directly to the sun for 10 days (June 6 to 16, 1931), and at the expiration of this time the transmissions were as indicated in figure 4. Beginning June 17 and continuing until October, the samples were continuously exposed under the filters.

The sample kept in the dark showed practically no recovery in transmission (at 302 mμ) during this experiment, which was continued to October 5, 1931.

The sample exposed under quartz continued to decrease in transmission until October when it was completely stabilized, as is shown by the subsequent exposure (no covering) through November 1932.

The sample under window glass became stabilized in transmission by July 12, or about 3 weeks in advance of the sample exposed under Corning G584 (fig. 4). Part of this delay in attaining equilibrium under the filter, G584, is due to the much lower intensity of the radiation at 365 mμ. On the other hand, as will be shown presently,

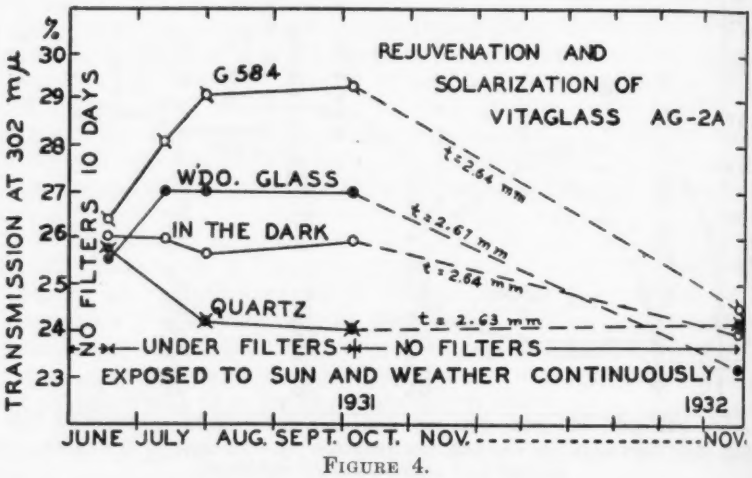

FIGURE 4.

the shorter wave lengths, transmitted by the filter of window glass, have the property of stabilizing the transmission at a much lower value than the longer wave lengths, at 365 to 405 mμ. Hence the equilibrium level in transmission, resulting from exposure under window glass, should be lower than that attained under the filter of G584 glass.

The sample under the filter G584 shows the greatest rejuvenation (by the wave lengths longer than about 330 mμ, as shown by fig. 1), the stabilization being practically complete by July 30, 1931, with but little increase in transmission by October 5, 1931, when the filter exposures were terminated. This effect of wave length upon the equilibrium level in transmission (photochemical action) is more clearly demonstrated by using homogeneous radiation, as described on a subsequent page.

These glasses were then mounted in the frames, regularly employed in studying solarization, and exposed directly to the sun and weather

continuously for a year. By the end of November 1932 the transmissions (at 302 mμ) were all reduced to the equivalent of about 24 percent (fig. 4) for a thickness of 2.64 mm. The transmission in this case is considerably lower then the average of the 15 samples shown in figure 2. This is probably owing to the fact that this particular lot of samples was from an early melt. It was found to be unusually photosensitive, and hence because of this sensitivity was chosen for investigation of the selective action of different wave lengths in changing the ultraviolet transmission.

This series of observations confirmed the earlier measurements in showing that the maximum rejuvenation in transmission (aside from that resulting from heat treatment) is produced by ultraviolet radiation of wave lengths in the region of 310 to 405 mμ.

(c) SERIES III

A further test of rejuvenation by wave lengths in the region of 450 mμ was made on two samples of Vitaglass which were first depreciated in transmission by exposure for 10 hours to the unfiltered radiation from the quartz mercury arc. The one sample was then exposed for 115 hours to the filtered radiation, principally of wave lengths 436 mμ and 546 mμ from the quartz mercury arc, isolated by means of a combination filter (of Noviol A and G584 glasses; fig. 1) which had a transmission of about 45 percent at 436 mμ.

To test the effect of the temperature alone the second sample, wrapped in black paper, was mounted adjacent to the sample under the glass filters, and similarly exposed to the lamp.

The results of this test verify the earlier observations, using filtered sunlight, showing an increase (see fig. 3, red glass) in transmission (at 302 mμ) as a result of exposure to filtered radiation of wave lengths longer than 405 mμ. In this test the increase amounted to 2 percent as compared with an increase of about 1 percent in transmission of the sample wrapped in black paper.

Apparently the wave lengths longer than 405 mμ, have a slight effect in rejuvenation; but this is not comparable with the highly selective action of the wave lengths in the region of 365 mμ. Since colorless glass has but little absorption in the region of 405 mμ only slight, if any, photochemical action by radiation of this wave length is to be expected.

3. EFFECT OF HOMOGENEOUS ULTRAVIOLET RADIATION UPON THE TRANSMISSION OF GLASS

The completion of an investigation of the physiological (erythemal) action of homogeneous ultraviolet radiation (14) released apparatus for a similar study of the photochemical action of these wave lengths upon the ultraviolet transmission of glass. The results of this study, using the experimental procedure described under caption II, are given in this subhead.

In a previous paper (10) it was shown that exposure to heterogeneous ultraviolet radiation changes (degrades or increases) the transmission throughout the whole ultraviolet spectrum investigated (250 to 400 mμ). Hence it was of interest to determine the effect of exposure to homogeneous radiation of a single wave length upon the ultraviolet spectral transmission. As shown in figure 5, the effect of exposure to homogeneous radiation, of different wave lengths, is to produce a

series of spectral transmission curves which are similar in outline but different in the magnitude of the transmission, depending upon the effectiveness of the different wave lengths in producing a stabilized photochemical change in the glass, the shortest wave lengths being the most effective. While this was no doubt to be expected, nevertheless, in view of the novelty of some of the herein recorded observations, it was desirable to verify our procedure of using the transmission for radiation of a single wave length, at 302 mμ, as a criterion for judging the photochemical change in glass (as described in caption II) which is exhibited as a change in transmission throughout a wide band of the ultraviolet spectrum.

In this connection it is relevant to add that the use of the emission line at 302 mμ as a means for studying photochemical change in glass, in which the substances undergoing a chemical change have wide over-

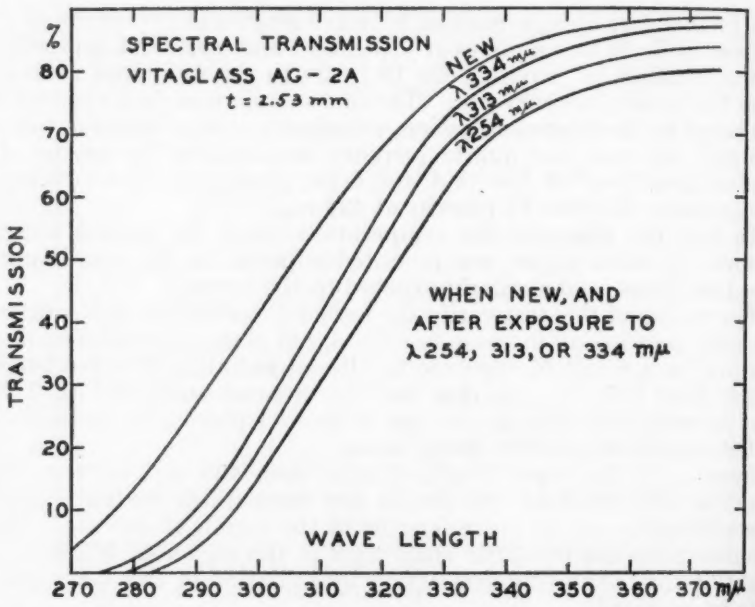

FIGURE 5.—*Effect of exposure to homogeneous radiation of different wave lengths upon the ultraviolet transmission of Vitaglass (a soda-lime-silica glass).*

lapping bands of absorption throughout the ultraviolet, is not to be construed as generally applicable, particularly in the study of substances having narrow bands of selective absorption (16).

(a) EFFECT UPON A SODA-LIME-SILICA GLASS

At the beginning of the observations the sample of Vitaglass (a soda-lime-silica glass containing iron oxide as an impurity) under examination had a transmission at 302 mμ of about 26 percent when completely solarized in sea level summer sunlight, figure 6. The transmission was further degraded, to about 21 percent, by exposure to the unfiltered radiation from the quartz mercury arc. The glass was then kept wrapped in black paper at room temperature several weeks before beginning the following series of observations using homogeneous radiation of measured intensities (microwatts per cm^2).

The result of the sequence of exposures to different wave lengths is illustrated in figure 6, in which the ordinates are percent transmissions at wave length 302 mμ and the abscissas are in billions (10^9) of

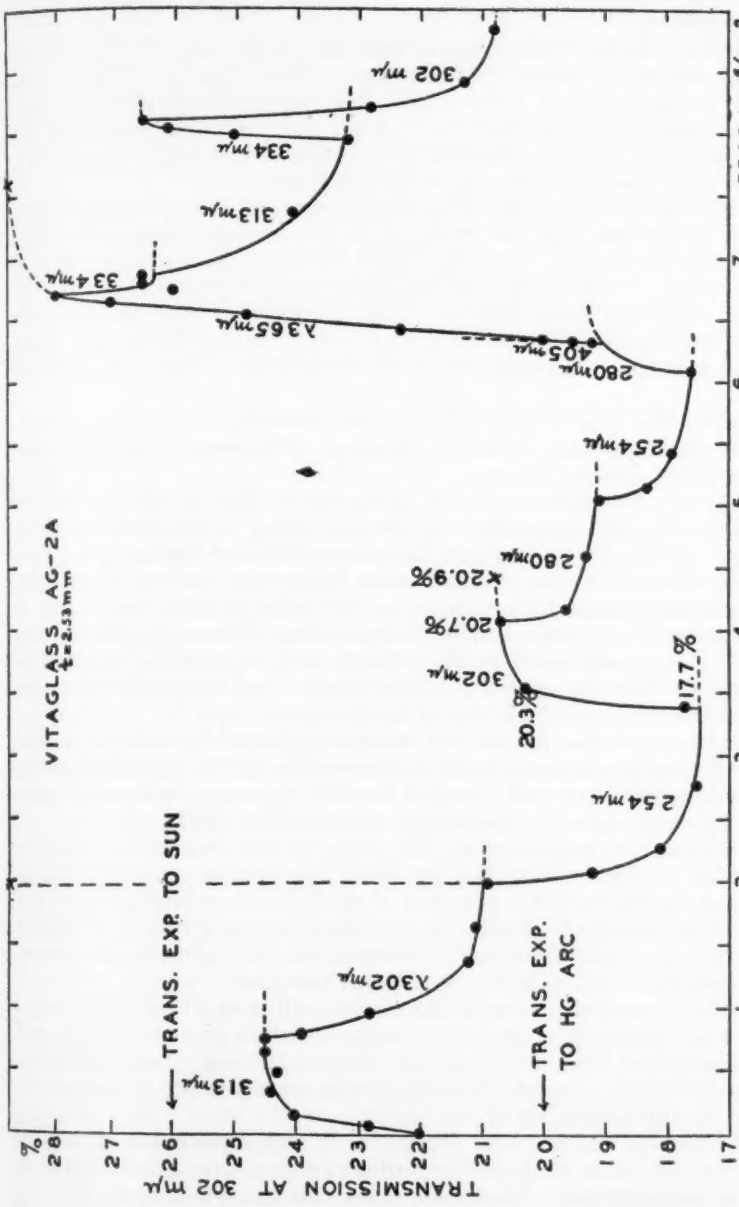

FIGURE 6.—*Equilibrium states in ultraviolet transmission as a function of the wave length of the radiation stimulus, depicted in the sequence of observation.*

ergs of the energy absorbed in the glass per cm² of the irradiated surface. These values are obtained from the intensity of the incident radiation and the average absorption during the interval of irradiation between two successive sets of transmission measurements.

The first exposure to homogeneous radiation of wave length 313 mμ increased the transmission from 21 to 24.5 percent. This is illustrated in figure 6 in which the dotted extensions of the curves are extrapolations showing how nearly the photochemical action appears to be completed.

The second exposure was made to wave length 302 mμ which reduced the transmission to about 20.9 percent. This was followed by an exposure to radiation of wave length 254 mμ which further reduced the transmission to 17.6 percent. After this, another exposure to 302 mμ restored the transmission to practically the value previously obtained with this wave length, at equilibrium.

At this stage of the experiment the transmission was again depreciated, in two steps, first by exposure to the emission line at 280 mμ (equilibrium transmission 19.2 percent), then by exposure to the line 254 mμ, which reduced the transmission to 17.6 percent previously obtained with this wave length. This shows that the shorter the wave length the lower the equilibrium level in transmission and that this is determined independently of the exposure to intervening wave lengths.

Following the exposure to 254 mμ the transmission was again restored to its previous equilibrium level, at 19.2 percent, by exposure to the emission line at 280 mμ.

An exposure was then made to the emission line at 405 mμ which has a relatively high intensity. However, owing to the small amount of energy absorbed by the glass, the photochemical change produced was slow, about 2 weeks of irradiation being required to obtain the 0.8 percent increase in transmission, as indicated in the illustration.

An exposure then made to the emission line of wave length 365 mμ increased the transmission to 28 percent, with a possible increase to 29 percent as observed on a duplicate sample used in another test and indicated by the dotted extension in figure 6.

The exposure to the line at 365 mμ was followed by a depreciation in transmission by exposure to the emission line at 334 mμ (equilibrium transmission, 26.5 percent), and a further decrease in transmission (to 23.2 percent) by exposure to the emission line at 313 mμ.

It is relevant to note that at this stage in the irradiation test the equilibrium transmission (23.2 percent) for exposure to 313 mμ is lower than the value (24.5 percent) observed at the beginning of the observations after exposing to the emission line at 313 mμ. Inspection showed that this decrease in transmission was not to be accounted for by a visible change in the surface of the glass.

After this second exposure to the emission line at 313 mμ the transmission was increased by exposure to the emission line at 334 mμ, and again depreciated by exposure to the line at 302 mμ, the equilibrium transmission (20.8 percent) reaching the same value (20.9 percent) as observed at the beginning of the series.

In addition to the tests on Vitaglass (a soda-lime-silica glass containing iron oxide as an impurity), observations were made also on a sample of iron-free soda-lime-silica glass (thickness=2.96 mm).[6]

The transmission at 302 mμ before exposure was 57 percent. After depreciation by exposure to the unfiltered radiation from the quartz

[6] Prepared by F. C. Flint of the Hazel Atlas Glass Co.

mercury arc the transmission was 40 percent. Further exposure to the quartz mercury arc under the filter G584 increased the transmission to 47 percent. Exposure then to homogeneous radiation of wave length 313 mμ for 35 hours decreased the transmission to 42.8 percent, showing that the pure soda-lime-silica glass as well as the impure glass has levels of photochemical stabilization which vary with the wave length of the activating radiation.

Evidently the observed photochemical action is in the pure soda-lime-silica portion of the glasses and not in the iron oxide impurities. There is no doubt but that the presence of the iron oxide lowers the transmission throughout the ultraviolet; but, comparing the results obtained on the iron-free glass with those on the glass known to contain iron, it does not appear that the iron oxide increases the photochemical action that occurs in the pure soda-lime-silica glass. If the iron oxide itself undergoes a photochemical change, as is commonly accepted, the products formed do not appear to produce a change in the ultraviolet transmission comparable to that observed in the relatively iron-free soda-lime-silica glass (23).

(b) EFFECT UPON A PHOSPHATE-LIME GLASS

A difficulty in studying the photochemical stability of ferrous and ferric iron in a soda-lime-silica glass arises from the fact that the ultraviolet absorption of the glass and of the iron oxide occurs in a wide spectral band, beginning at about 350 mμ and extending to an unknown wave length shorter than 280 mμ.

It is therefore of interest to include some observations on the change in transmission of Corex-A glass which is known to contain a small amount of iron oxide as an impurity, but which, in the unsolarized condition, has a high transmission throughout the region of 250 to 320 mμ (10).

Radiation of wave lengths 295 to 313 mμ from the sun does not affect the ultraviolet transmission, but shorter wave lengths, from a quartz mercury arc, produce a marked decrease in ultraviolet transmission in the region of 250 to 365 mμ, the resulting transmission curve having some resemblance to that of the soda-lime-silica glass (10).

The main constituent of Corex-A Glass is fused calcium phosphate, with the oxides of Al, B, Mg, Na, Si, and Fe as minor constituents (13). The iron oxide content reported by Starkie and Turner (13) is of the order of 0.03 percent.

In the present work the ultraviolet spectral transmission of an optically polished sample of Corex-A glass, 3.67 mm in thickness, (see fig. 7), new, and after exposures of 17 and 34 hours, was depreciated by exposure to the unfiltered radiation of a high potential mercury vapor arc [7] discharge in which the ultraviolet radiation of wave lengths shorter than 313 mμ is confined almost entirely (95 percent) to the resonance emission line at 253.7 mμ. After being kept in the dark for 12 days, during which the transmission at 302 mμ increased a small amount (from 21.5 to 22.2 percent), the glass was exposed for 22 hours to homogeneous radiation of wave length 313 mμ, with no appreciable change in transmission.

The glass was then exposed for 48 hours to the emission line at 365 mμ without producing a measurable change in transmission. This

[7] The "Sc-2537 tube", made by the Research Lab., Hanovia Chemical and Manufacturing Co.

is remarkable in view of the fact that a similar exposure of Vitaglass (a soda-lime-silica glass) for the same length of time would have raised the transmission about 9 percent, or to practically the equilibrium level (29 percent), indicated in figure 6.

As already noted, Corex-A (a phosphate) glass is interesting because the main constituents have little or no absorption in the region of 280 to 350 mμ in which the photosensitive substance undergoes a photochemical change. After depreciating the transmission by radiation of wave length 254 mμ it has not been possible to reverse the photochemical action by means of the wave lengths at 302 to 365 mμ. It would be interesting to determine whether the wave length at 254 mμ reverses the action of the emission lines at 200 mμ and shorter wave lengths (easily obtainable by using the spark

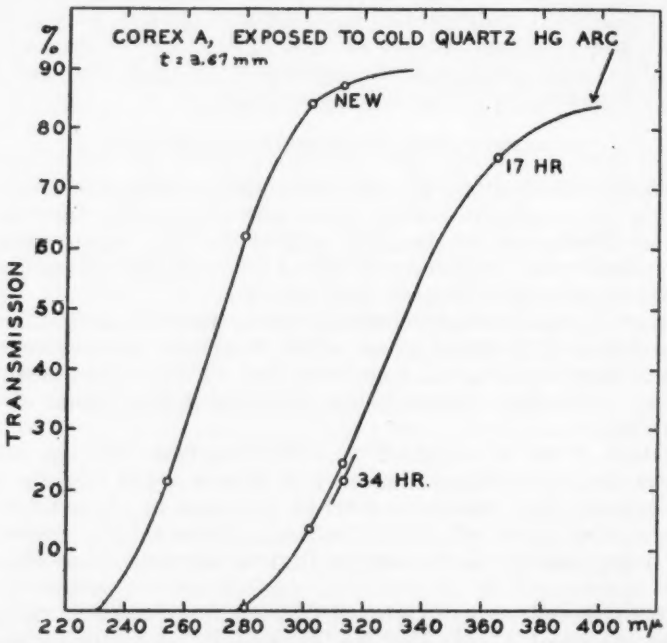

FIGURE 7.—*Effect of exposure of Corex A (a phosphate glass) to radiation, chiefly of wave length 253.7* mμ.

discharge between electrodes of Zn and of Al); but to determine the transmission at these short wave lengths it would be necessary to use very thin samples of glass.

4. SPONTANEOUS RECOVERY IN TRANSMISSION

It was of interest to determine the change in transmission of the irradiated as compared with the unirradiated portion of a sample of glass kept in the dark at laboratory temperature after a 10-hour exposure of a small area to the unfiltered radiation from a quartz mercury arc. For this purpose the central portion (suitably marked), 2 mm wide and 15 mm long, of a sample of Vitaglass was irradiated and the transmission measured by moving the exposed and the adjacent unexposed area laterally across the spectrometer slit, which was 0.6 mm in width. The wave length 313 mμ was used in the

transmission measurements because of the higher intensity, which increased the accuracy, and with fewer observations shortened the time of exposure necessary for making the measurements.

As shown in figure 8, the difference in transmission at wave length 313 mμ between the unexposed and the freshly exposed portion was (50.5—36.5=) 14.0 percent. After being kept in the dark for 2, 7, and 12 months the difference in transmission was found to have decreased respectively to 11, 8.5, and 9 percent.

During an interval of 7 months' storage after exposure (at laboratory temperature) there is a spontaneous recovery of about 4.5 percent (36.5 to 41.0 at 313 mμ) in the transmission of the exposed part. During the comparatively short time required for the transmission measurements, the sample was exposed to the unfiltered radiation of the mercury arc, and the solarization resulting from this on the

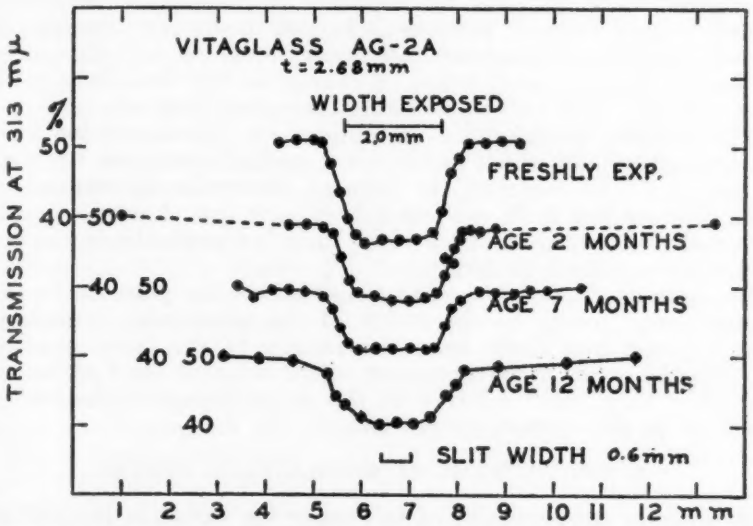

FIGURE 8.—*Spontaneous recovery in transmission of a sample of Vitaglass depreciated by exposure to ultraviolet radiation, then kept in the dark, at room temperature.*

"exposed" part is unquestionably negligible. Whether the 1 percent lower transmission of the unexposed part is owing to depreciation during observations is unknown.

The spontaneous recovery in transmission of this sample no doubt explains part of the observed increase in transmission of the sample exposed to the sun under red glass (fig. 3) which after exposure to the lamp and before exposure under the glass had practically the same transmission as this sample (18 to 19 percent) at 302 mμ. On the other hand, the sample (fig. 4) from the same plate which had not been so strongly irradiated (transmission reduced to 26 percent at 302 mμ) changed but little in transmission during the 3 months' storage after exposure, which is probably to be expected.

The spontaneous recovery of a substance that has undergone a photochemical change by exposure to ultraviolet radiation has become a well-known phenomenon. The object of the present observations was to inquire into this question relative to glass, which, being

a solid solution, shows no appreciable widening of the area of photochemical action by diffusion out from the region exposed. This is well illustrated in the lower part of figure 8, "age 12 months."

The spontaneous recovery in transmission (fig. 8) amounting to about 4.5 percent at 313 mμ in 7 months corresponds to about 4.0 percent (actual transmission 18 to 22 percent) at 302 mμ. From this it may be seen that the spontaneous recovery in transmission (amounting to 0.5 percent per month) during the irradiation, as in figure 6, is small and is overshadowed when the glass is exposed to wave lengths which depreciate the transmission

IV. DISCUSSION OF DATA

In the absence of a chemical analysis of the small quantities of the products formed in glass by exposure to ultraviolet radiation of different wave lengths, recourse is had to a physical (spectroradiometric) analysis of the absorption spectrum, which is a characteristic of every substance and, hence, a change in this is indicative of a change in the chemical composition of the glass by irradiation.

The present investigation is confined to the absorption in the extreme ultraviolet which undergoes a marked change on irradiation of the glass. In contrast, the infrared absorption spectrum of the glass changes but little, on irradiation; and this change is confined principally to the region of 1 μ where there is a weak absorption band, commonly ascribed to ferrous oxide.

Incidentally, it is relevant to note that as the glass decreases in transparency, owing to the action of the ultraviolet radiation in changing the iron oxide from the ferrous to the ferric condition, the glass increases in transparency to the infrared (at 1 μ); but this change is very small relative to the large change in transmission observed in the extreme ultraviolet.

1. PHOTOCHEMICAL EQUILIBRIUM STATES

As noted in the beginning of this paper the variation in ultraviolet transmission is an indication of the magnitude of the photochemical change produced in a glass on exposure to ultraviolet radiation of certain wave lengths. After exposure to radiation of a given wave length for a sufficient length of time, there is no further change in transmission, indicating that an approximate photochemical equilibrium is established.

(a) A SODA-LIME-SILICA GLASS

As shown in figure 6, for each wave length of the exciting radiation there is an equilibrium value in the transmission (i.e., of the photechemical action), the direction of the change in transmission to attain this equilibrium level depending upon the existing condition or state of the glass. The shorter the wave length (between 254 and 365 mμ) of the homogeneous exciting radiation, the lower the equilibrium value of the transmission.

If the ultraviolet transmission is below the equilibrium value, as a result of previous exposure to wave lengths shorter than the one under consideration, prolonged exposure to this wave length increases the transmission to the equilibrium value. On the other hand, if by heat treatment or by exposure to wave lengths longer than the

one under consideration, the transmission is raised above the equilibrium value for this wave length, then exposure to this wave length decreases the transmission to the equilibrium value (19). In other words, for each wave length, the photochemical reaction in an ordinary soda-lime-silica glass is reversible, the direction of the reaction depending upon the existing condition or state of the glass.

By extrapolation of the various curves of appreciation and depreciation in transmission, as indicated by the dotted parts of the curves depicted in figure 6, it is possible to obtain the approximate equilibrium value of the transmission for each wave length of the exciting radiation used, and to obtain an indication of the relative magnitude of the photochemical change involved in passing from one of the corresponding photochemical equilibrium states to any one of the others.

As shown in figure 9 the transmission equilibrium (thickness of glass 2.53 mm) rises from about 17.5 percent for wavelength 254 mμ to about 29 percent for wave-length 365 mμ. The higher of the two points at 313 mμ was obtained in the first part of the cycle of exposures, and apparently does not belong with the other data. As already mentioned, the glass appears to have undergone a permanent change in transmission—a question that will require further investigation.

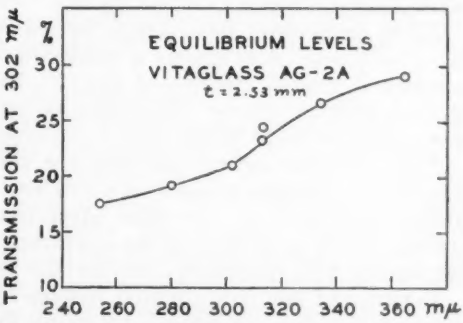

FIGURE 9.—*Equilibrium states in ultraviolet transmission after exposure to homogeneous radiation of different wave lengths.* (See fig. 6.)

One sample which had been subjected to heat treatment at 500° C and subsequently exposed to wavelength 365 mμ (also a duplicate sample exposed under a filter opaque to practically all radiation shorter than 365 mμ) decreased several percent in transmission upon 100 hours continued exposure. The decrease in transmission was rather slow, but the data indicated the possibility of either a small permanent change in the glass or else an equilibrium level slightly above 29 percent.

The logical procedure would have been to make a thorough examination of photochemical equilibrium states in a soda-lime-silica glass that is as free as possible from contamination with iron oxide. However, the first step was to establish the reality of the photochemical equilibrium levels. After this, the filter method can replace the slow process of stabilization by isolated spectral lines. In this manner (as already mentioned), by using filters it has been established that this photochemical reaction occurs in the purest iron-free samples of soda-lime-silica glass yet examined. The evidence at present available indicates that this remarkable photochemical change occurs in the soda-lime constituent and that the change, if any, in the iron oxide is an additional reaction (23).

In this connection, it is relevant to record transmission tests on samples of bottle glass (a soda-lime-silica glass, decolorized with manganese) that were colored a deep amethyst, as a result of exposure

to the sun. An additional exposure to the unfiltered, short wave length radiation from the quartz mercury arc decreased but little the ultraviolet transmission (10). On exposure of this sample to filtered radiation (principally of wave length 365 mμ) from the quartz mercury arc lamp, the ultraviolet transmission was appreciably increased. This is in agreement with the observations on the soda-lime-silica glasses that had not been decolorized.

(b) A PHOSPHATE-LIME GLASS

In contrast with soda-lime-silica glasses, which, even in their purest state, show an appreciable absorption at 350 mμ, and which, in thicknesses of 2 mm, are practically opaque to radiation of wave lengths shorter than 280 mμ, Corex A (a phosphate glass containing a small amount of iron oxide as an impurity or nonessential constituent) before irradiation, is highly transparent to radiation of wave lengths longer than 280 mμ. (See fig. 7.) Apparently the behavior of iron oxide in a phosphate glass is different from that observed in soda-lime-silica glass. (See fig. 5.)

After prolonged irradiation by wave lengths shorter than 280 mμ the phosphate glass shows a reddish color, and the ultraviolet transmission is greatly decreased (fig. 7), but whether the absorbing substance, with its strong absorption at 365 mμ and shorter wave lengths, is an oxide of iron (ferric oxide) remains to be determined.

The outstanding conclusions are that exposure of the previously irradiated phosphate glass to wave lengths (302 to 365 mμ) which are highly absorbed by the glass after irradiation, does not restore the transparency as it does in the soda-lime-silica glass and that only heat treatment will (partially) restore the transmission (10) (11).

Because of the complicated nature of the results, this whole investigation is being continued, by using different combinations of materials in the glass, and by using filter methods to facilitate the photochemical tests.

2. RELATION BETWEEN THE TRANSMISSION AND THE INTEGRATED ENERGY ABSORBED

In figure 6 the abscissas represent the total radiant energy absorbed in the glass, no distinction being made between the amount absorbed by the main constituents of the glass [8] and the amount absorbed by the photosensitive substance which undergoes the photochemical reaction (indicated by the change in transmission) because at this stage of knowledge of the subject, no distinction as to the amount absorbed by the different components seems justifiable.

The abscissas in figure 6 represent all the energy absorbed in the glass in changing from one equilibrium level to another. The curves serve the purpose of depicting our observations in a connected manner, but without further data they cannot be used to elucidate several important questions. For example, the rate of transition in going from one equilibrium level to another depends upon the starting point and cannot be determined directly from the data illustrated in figure 6.

The slopes of the transmission curves (e. g., for the 365 mμ line and the 254 mμ line) are not comparable, because one is at the initial

[8] Whether and to what extent the constituents Na_2O and CaO are affected by ultraviolet radiation, and the role of iron oxide and free oxygen, remains undetermined (23).

stage and the other is at the final stage of the reaction. The slope of the recovery curve using the 365 mμ line appears steeper than the depreciation curve using the 254 mμ line. However, if the latter curve had been observed beginning at the equilibrium level at 29 percent, as indicated by the dotted line in figure 6, the slope of the initial part of this transmission curve might be just as steep as that of the 365 mμ emission line at its initial stage (22).

Manifestly, as indicated in figure 6, the total energy required to attain equilibrium depends upon the history of the photosensitive material. From an inspection of the sections of the curves in figure 6, it appears that the total energy absorbed in going from one equilibrium level to a lower equilibrium level is greater than that absorbed in returning to the original equilibrium level. Further investigation is required to determine whether this is generally true and whether it is owing to a difference in the heat of formation and heat of disassociation of the photosensitive substance.

In figure 5 the spectral transmission curves marked "new", and particularly the curve marked "334 mμ", are typical of soda-lime-silica window glasses, whether or not they contain a photosensitive substance that changes in transmission on exposure to ultraviolet radiation.

From these curves it can be seen that the main constituents of the glass are almost completely opaque to radiation of wave lengths 280 mμ and shorter, whereas at wave lengths longer than 365 mμ (to 405 mμ, not illustrated in fig. 5) only 2 to 3 percent of the incident radiation is absorbed by the glass. From this it can be seen that, for wave lengths 254 mμ and shorter, the depth of penetration is shallow and that the greatest photochemical action occurs near the surface of the glass facing the incident radiation. On the other hand, for the wave lengths 365 mμ and longer, the penetration is deep and, during the process of formation and disintegration of the photosensitive substance, the concentration is more uniform throughout the irradiated layer of glass.

In view of the foregoing considerations it is evidently desirable to obtain some idea of the energy relations involved directly in the photochemical reactions. Without a chemical analysis data are lacking regarding the concentration of the photosensitive substance. The only reference points are the equilibrium states where (as evidenced by the constant value of the transmission) no further chemical change is produced by a given wave length, and the energy absorbed is apparently converted into heat, just as occurs in any glass not containing a photosensitive material. Using these equilibrium levels as reference points, and using the changes in transmission as a measure of changes in concentration, calculations are in progress on the energies involved in the formation and disintegration of the photosensitive substance. We hope to be able to report further on this subject.

In concluding the discussion under this caption it is to be noted that contrary to earlier reports, in our examinations of samples of soda-lime-silica glass, prepared from materials practically free from iron oxide, a depreciation in transmission was observed. While the stabilized transmission at 302 mμ was much higher than that of similar glasses containing a small amount of iron oxide, the percentage change in transmission on solarization was about the same for

the two kinds of glass. This is in agreement with some of the earlier observations on various kinds of special window glasses (10). In this connection, it is relevant to note that Starkie and Turner (13) found that the ratio of the ferrous oxide to the total iron oxide was fairly uniform over a relatively wide range of concentrations of iron oxide in the glass.

As a final remark it is relevant to note that, in the spectral range investigated, the shortest and the longest wave lengths have the power to produce the greatest photochemical changes; the former in depreciating, the latter in appreciating the transmission of a soda-lime-silica glass.

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23. As stated on page 776, footnote 2, samples of (relatively iron free) soda-lime-silica and soda-silica glasses, prepared from pure materials, in a platinum crucible (heated in an electric furnace), exhibit stages of photochemical equilibrium, as observed in the window glasses. In contrast, a similarly prepared sample of potash-lime-silica glass, which in a thickness of 2.6 mm is highly transparent to the ultraviolet (transmission 16 percent at 254 mμ) was not appreciably affected by ultraviolet radiation. From the observations on these three kinds of glass it appears that soda is the photosensitive constituent in a soda-lime-silica glass.

WASHINGTON, D. C., May 15, 1934.

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ISOLATION OF A NONANAPHTHENE FROM AN OKLAHOMA PETROLEUM [1]

By Joseph D. White [2] and Frank W. Rose, Jr.[2]

ABSTRACT

A nonanaphthene boiling at 136.65° C has been isolated from an Oklahoma petroleum. This has been accomplished by fractional crystallization, from a solution first in liquid propane and methane, and then in dichlorodifluoromethane, of the distillate boiling normally between 136 and 137° C after first removing the aromatic hydrocarbons present. Its boiling point, freezing point, density, refractive index, heat of fusion, and critical solution temperature in aniline have been determined.

Its empirical formula of C_9H_{18} has been established, but its structural formula is not known. It is probably a derivative of cyclopentane. There is a remote possibility that it is a mixture of stereoisomers. It constitutes not more than 0.1 percent of the crude petroleum.

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I. INTRODUCTION

The term "naphthenes" was used by Markownikoff and Ogloblin [3] to designate those compounds occurring in petroleum which belong to the class of saturated monocyclic hydrocarbons having the empirical formula C_nH_{2n}. Those found in the lighter distillates of petroleum are chiefly the alkyl derivatives of cyclopentane and cyclohexane.

A "nonanaphthene" is a naphthene containing 9 carbon atoms. The one herein described is probably a derivative of cyclopentane, as will be pointed out later. It was found in the fraction of an Oklahoma petroleum which distilled normally between 135 and 137° C and was separated from other constituents by physical means.

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project No. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associate at the National Bureau of Standards representing the American Petroleum Institute.

[3] Ber. Deut. Chem. Ges. **16(B)**, 1873 (1883).

II. PROCEDURE AND RESULTS

1. PRELIMINARY FRACTIONATION

The petroleum used in this work [4] was first systematically distilled, under the direction of S. T. Schicktanz, through the fractionating columns developed at this Bureau.[5] The distillation procedure varied for successive stages in the rectification. The final distillation was made in resistant glass stills having 30-plate columns, using a reflux ratio of 10:1 and a rate of about 1 ml/min—the distillate being separated into fractions for each degree rise in its boiling point. Figure

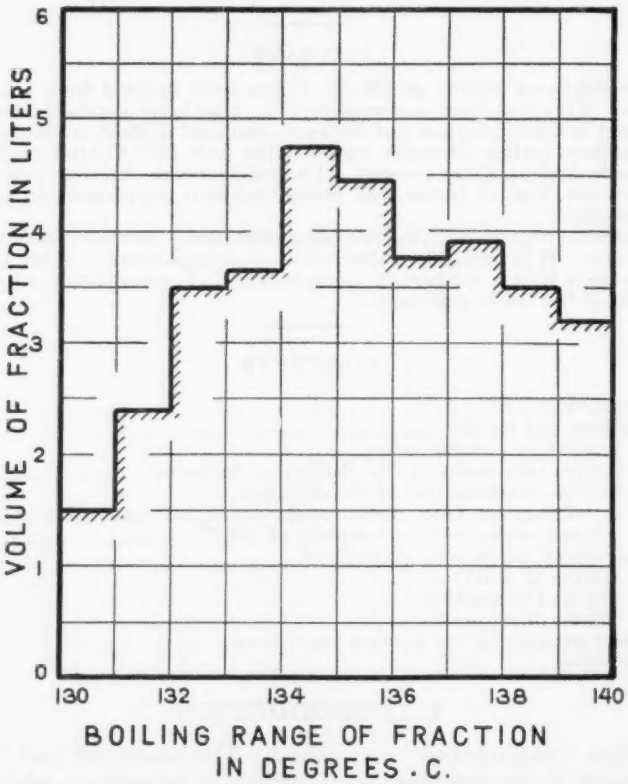

FIGURE 1.—*Volume distribution of petroleum fractions boiling between 130 and 140° C before removing any constituents.*

1 shows graphically the distribution by volume with respect to boiling range of the 35 liters distilling between 130 and 140° C. A large fraction which concentrated between 134 and 136° C is represented by a volume peak on the distillation graph.

All of the petroleum which boiled between 130 and 145° C was extracted with liquid sulphur dioxide to remove most of the aromatic hydrocarbons.[6] The residue was then distilled and extracted again. Following the second extraction, the immiscible portion was finally

[4] A description of the oil is given in BS J. Research **2**, 469, table 1 (1929) RP45.
[5] BS J. Research **2**, 470 (1929) RP45; **6**, 378 (1931) RP282; **7**, 851 (1931) RP379.
[6] BS J. Research **9**, 714 (1932) RP501.

distilled, once at atmospheric pressure and 3 times at a pressure of 215 mm Hg, using the 30-plate columns as before but separating the distillate into 0.5° C cuts. In graph I of figure 2 the volume of each of these cuts is plotted against the boiling range. The boiling points indicated are those for a pressure of 215 mm Hg, the range 88 to 98° C corresponding approximately to the range 130 to 140° C at

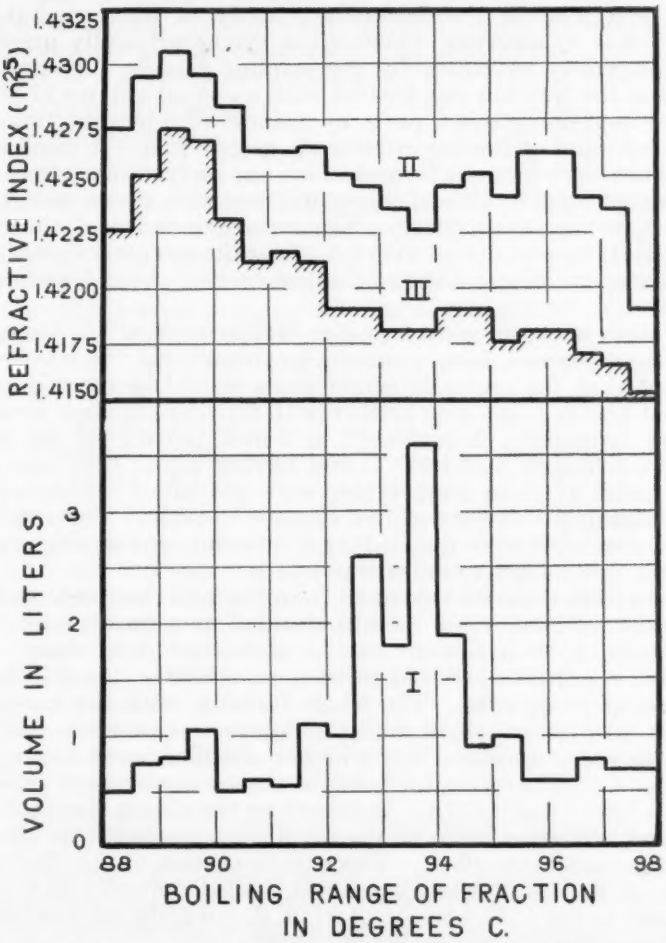

FIGURE 2.—*Volume distribution and refractive indices, with respect to boiling range at 215* mm, *of the petroleum fractions after extraction with sulphur dioxide and redistillation.*

Graph I, volume distribution; graph II, refractive indices; graph III, refractive indices after subsequent treatment with concentrated sulphuric acid.

760 mm Hg. The total volume of oil boiling in this region, after removing the aromatic constituents, was about 20 liters.

The largest single cut from the distillation was the 3.6 liters boiling between 93.5 and 94° C. Apparently a compound, or a constant-boiling mixture, had concentrated here. Its refractive index of 1.4227 [7] marked a minimum on the refractive index curve shown in

[7] The refractive indices throughout this paper are given for the D-line of sodium, and for a temperature of 25° C.

graph II of figure 2. This index was intermediate in value between those for the isononanes and nonanaphthenes known to boil near this temperature, a fact suggesting that the distillation fraction was a constant-boiling mixture composed of such hydrocarbons.

2. PRELIMINARY STUDY OF THE DISTILLATION FRACTIONS

The first step in the preliminary study of the constant-boiling mixture was to ascertain whether the xylene originally present had been completely extracted by the sulphur dioxide. Accordingly, a sample of the fraction was treated with an equal volume of nitrating mixture containing equal parts by volume of 3-percent fuming sulphuric acid and of fuming nitric acid, sp gr=1.50. A small amount of solid nitro-product was formed which was recrystallized from alcohol and treated further with nitrating mixture on a steam bath to yield the 2, 4, 6-trinitro-*m*-xylene. The refractive index of the residual oil was 1.4172 as compared with 1.4227 for the sample before nitration. This change in index indicated the presence of about 7 mole percent of xylene.

Nitration tests on other fractions boiling near 94° C showed that they also contained some aromatic hydrocarbons. It was therefore apparent that the aromatic constituents should be more completely removed before proceeding further with the identification or analysis of what remained. Accordingly, a 2-liter portion of the fraction boiling between 93.5 and 94° C and having $n_{25}=1.4226$ was stirred for 24 hours at room temperature with 400 ml of fuming sulphuric acid containing 3 percent of free sulphur trioxide. The residual oil, after separating it from the acid layer, washing, and drying, measured 1850 ml. Its refractive index was 1.4179.

To ascertain if the oil recovered from the acid treatment could now be further rectified, 1,800 ml was distilled at a pressure of 215 mm Hg through a 10-m column packed with steel jack chain. Under operating conditions believed to be most effective, the distillate was collected in 75-ml cuts. The whole fraction, with the exception of the first 10 percent which boiled a degree or two lower and whose refractive index averaged 0.003 higher, distilled over between 93.7 and 94.0° C. The refractive index of the successive cuts varied only between 1.4171 and 1.4176. As judged by the almost constant boiling point and refractive index of the distillation fractions, no significant separation had taken place. The middle portion of the distillate (80 percent of the total) when combined, boiled normally in a Cottrell apparatus at 136.1° C, had $n_{25}=1.4173$, $d_{15}=0.760$ g/ml, and congealed to a vitreous solid when cooled to −140° C.

The action of chlorosulphonic acid upon this material was observed to see if it would have a selective action on any constituent present, and thus effect a separation. A 10-ml sample of the oil was treated successively with 5 portions of the acid in 5-ml lots. Reaction with each portion was equally vigorous, the acid layer turning dark amber in color. The treatment was continued until half of the oil was destroyed. The remainder, when washed and distilled, had a refractive index of 1.4161, compared with 1.4173 for the original. Apparently, if the oil was a mixture of naphthene and paraffin hydrocarbons both classes were almost equally attacked.

When a sample of the distillate was cooled slowly, it would not crystallize. At −143° C it had become a clear, highly viscous, semi-solid mass. Obviously, then, the mixture of hydrocarbons could not be separated by crystallization from the oil itself. When, however, the oil diluted with twice its volume of propane was cooled and allowed to stand, a crystalline mass slowly developed, which at −140° C was exceedingly fine and pasty in texture. On whirling the mass in a centrifuge, crystals remained in the basket which were still pasty and contained a large amount of occluded propane. On removing the propane, the refractive indices of the fractiens were as follows:

Crystal fraction	=1.4196
Mother liquor	=1.4166
Original oil	=1.4173

The higher refractive index of the crystal fraction was evidence that a naphthene hydrocarbon was concentrating in the solid phase.

When a mixture consisting of equal volumes of oil and propane was precooled to about −150° C and then added dropwise to a quantity of liquid methane equal in volume to the oil-propane mixture, crystals of good texture appeared which were separated from the liquid phase by centrifuging. After removing propane and methane, the different fractions had the following refractive indices:

Crystal fraction	=1.4219
Mother liquor	=1.4125
Original oil	=1.4173

It was apparent, from the large difference in refractive index between the crystal fraction and mother liquor, that a pronounced separation had taken place and that a systematic crystallization from a solution in liquid propane and methane by the procedure described by Leslie [8] would be an effective method for further separating the distillation fraction into its constituents. Using this procedure, there was obtained from the distillate a 100-ml fraction having the following properties: bp 760=136.7° C, fp=−78.5° C, n^{25}_D=1.4257, d_{25}=0.775 g/ml. The material was chiefly a naphthene, as indicated by its odor, density, and refractive index, but it was still impure as judged by the fact that it froze over a range of several degrees.

3. FURTHER FRACTIONATION OF THE DISTILLATE

Before attempting to isolate more of the detected naphthene, the distillation fractions shown in figure 2 were treated to free them more completely from aromatic hydrocarbons. The refractive indices of the fractions after this treatment are shown in graph III of figure 2. It may be observed in the figure that the indices for some of the fractions were thus lowered by about 0.005, corresponding to about 7 mole percent of aromatic hydrocarbons. For the fractions boiling near the boiling points of *p*- and *m*-xylene (about 97° C at 215) a greater lowering in refractive index was produced, amounting in the case of the 96 to 97° C cut to 0.008. This corresponds to a xylene content of about 10 mole percent. The analysis was borne out by a corresponding reduction in volume of the oil on treating with sulphuric acid.

[8] BS J. Research **10**, 609. (1933) RP552

In an effort to concentrate the naphthene further by distillation, the nine liters of acid-treated material, boiling between 93 and 95.5° C, was redistilled through 3-m columns packed with jewelers' locket chain.[9] The distillation was carried out under atmospheric pressure, in the presence of carbon dioxide gas, with a reflux ratio of about 20:1, and at a rate of 0.5 ml per minute. The distillate was collected in 50-ml cuts which were sorted and blended according to their boiling points and refractive indices. As a result the four blended fractions listed in table 1 were obtained.

TABLE 1.—*Properties of blended fractions obtained by distilling the acid-treated material boiling between 93 and 95.5° C at 215 mm through columns packed with locket chain.*

Fraction	Volume	Boiling range (760)	n^{25}_D range
	ml	° C	
1	2850	135 to 136.0	1.4110 to 1.4135
2	1100	136.0 to 136.8	1.4135 to 1.4215
3	3850	136.8 to 137.0	1.4215 to 1.4230
4	1100	137.0 to 138	1.4224 to 1.4215

The first fraction was composed chiefly of isononanes. Work on its separation is now in progress. The fourth fraction consisted for the most part of a mixture of naphthenes. This was shown by the fact that when the material was fractionally crystallized the resulting fractions differed widely in freezing points (indicating a marked difference in composition) but possessed nearly the same relatively high refractive index. The second fraction of distillate was intermediate in composition between that of the first and third. The large volume of the third fraction (nearly 4 liters), its narrow boiling range, and its high refractive index, made it clear that here was a fraction highly concentrated in naphthenes.

Systematic crystallization of this 4 liters of material, boiling between 136.8 and 137° C, from a propane-methane solution yielded finally a series of fractions grouped according to table 2.

TABLE 2.—*Properties of some crystallization fractions*

Group	Volume	n^{25}_D	Boiling range	Freezing range
	ml		° C	° C
1	200	1.4271	136.65 to 136.7	−71 to −74
2	300	1.4255 to 1.4267	136.7 to 136.8	−75 to −80
3	200	1.4250 to 1.4255	136.8 to 136.9	−80 to −90

The mother liquor left from the crystallization had an average refractive index of 1.4223, boiled slightly higher than the listed fractions, and could not be further separated by crystallization. When it was redistilled, the successive fractions of distillate varied in boiling point from 136.8 to 137.3° C. The refractive index reached a maximum of n_{25}=1.4233 for the cut distilling at 137.1° C. The fractions

[9] S. T. Schicktanz, BS J.Research **11**, 89 (1933) RP579.

with boiling points below 137.0° C could be fractionated by crystallization; those boiling at and above 137.0° C could not. This fact indicates that the material boiling at this temperature was a mixture of naphthenes approaching their eutectic in composition. It was preserved for further separation at a future time.

4. CRYSTALLIZATION FROM DICHLORODIFLUOROMETHANE AND THE ISOLATION OF A NAPHTHENE BOILING AT 136.7° C

The moderately high melting point of the fractions, obtained by crystallization from solution in propane and methane, now made it possible to fractionally crystallize them further by a simpler method. Thus, preliminary experiments showed that when fractions having a refractive index of $n_{25} \geqq 1.423$ and boiling within a few tenths of a degree of 136.7° C (i. e., 136.5° to 136.8° C) were mixed with an equal or smaller volume of dichlorodifluoromethane and cooled, crystals of good texture would form which could be readily separated by centrifuging. Such mixtures froze initially at about −90° C for fractions having a refractive index of $n_{25} \geqq 1.4260$, at −135° C for a fraction with $n_{25} = 1.4230$. A good crop of crystals was produced at a point 10° below the initial freezing point. The growth of crystals was slow, some time being required for "incubation" without stirring in order to get crystals of good texture instead of an amorphous mass. When crystallized in the manner described, the frozen material could then be fractionated further by allowing it to melt slowly in a centrifuge having a basket with an open top which permitted its contents to be stirred.

Systematic crystallization of the concentrated naphthene fractions from solution in dichlorodifluoromethane[10] coupled with fractional distillation finally produced a 200-ml sample of the naphthene which, after refluxing for 1 hour over sodium to remove all traces of solvent, was distilled and used for a study of its properties. It boiled at 136.7° C, melted between −66.3° and −65.7° C, had $n_{25} = 1.4273$, and a density at 20° C of 0.7788 g/ml.

III. PROPERTIES OF THE ISOLATED NAPHTHENE

1. DEGREE OF PURITY

Before presenting an array of physical constants which will serve to identify a fraction of petroleum as a certain hydrocarbon it is first necessary to prove that the given fraction is substantially a single substance, not a mixture. As to purity of a sample of oil containing a known hydrocarbon one can be guided by comparing its physical constants with those of a sample of the pure material. In the case of an unidentified hydrocarbon this cannot be done. It then becomes necessary for evidence of purity to rely upon the vaporizing and freezing behavior of the substance.[11]

As a vaporizing test the distillation range of the 200 ml-sample, isolated by crystallizing from dichlorodifluoromethane, was determined by distilling it very carefully through a small, highly effective fractionating column and noting the boiling point of each successive 40 ml of distillate. The refractive index and melting range of the

[10] The dichlorodifluoromethane was furnished us through the courtesy of Kinetic Chemicals, Inc., Wilmington, Del. It boils at −30° C, remains limpid at low temperatures, and is nonflammable.

[11] Tests of this kind have been outlined by Washburn, Ind. Eng. Chem. **22** 985 (1930).

fractions were also measured. The data for the first, middle, and residual fractions are recorded in table 3. The values are not absolute and are tabulated for comparative purposes only.

TABLE 3.—*Properties of fractions from the vaporizing test*

Fraction	Boiling point 760 mm	Melting point range		n_D^{25}
		Initial	Final	
	°C	°C	°C	
First	136.70	−66.4	−65.5	1.4272
Middle	136.70	−66.3	−65.6	1.4273
Residue	136.73	−66.8	−65.8	1.4273

From the data it is evident that each fraction of distillate had essentially the same values for the physical properties determined.

For the purpose of observing the behavior of the naphthene on cooling, the fractions from the distillation test were recombined, the whole

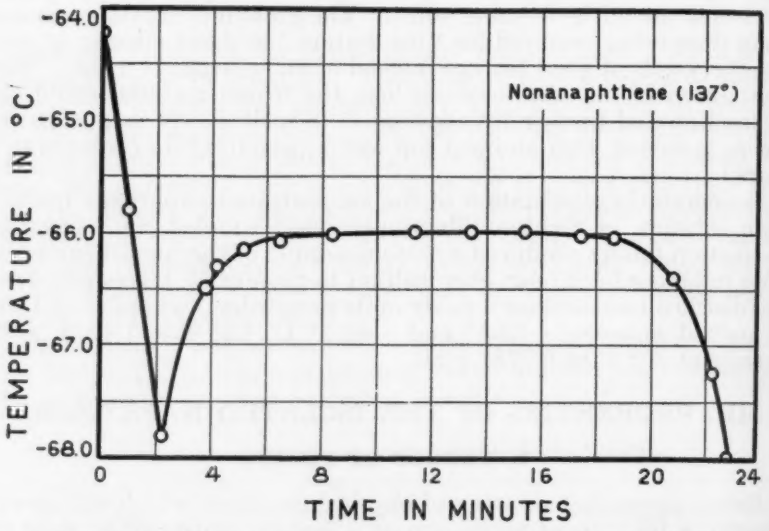

FIGURE 3.—*Time-temperature cooling curve of the nonanaphthene.*

sample frozen without solvent, and fractionated by melting. The last quarter to melt was used for the freezing test. In figure 3 is recorded the time-temperature cooling curve for the recrystallized sample. The prolonged halt in temperature, as shown by the region in the curve parallel to the time axis indicates that the sample froze almost entirely at a constant temperature.

The behavior of the material on distilling and freezing indicated that it was either a nearly pure substance or a mixture which was nearly constant-boiling and constant-freezing. Mixtures of the constant freezing type may be either eutectic mixtures or those forming solid solutions of components having the same or substantially the same freezing point. To see if an examination of the isolated material in the solid state would yield some information about its composition,

the growth and dissolution of its crystals were observed under the microscope.[12] On freezing, the hydrocarbon at first supercooled greatly and crystals which appeared were so fine-grained that interpretation of their nature was impossible. When, however, the crystals were allowed to melt almost completely and the material was slowly refrozen, the solid which persisted prevented a large amount of supercooling. The crystals which formed under these conditions were much larger, were composed of a single solid phase, and continued to grow until all was frozen. On melting, all crystals in a given region disappeared rapidly and apparently with the same velocity. Crystals were also produced by cooling a solution of the naphthene in an equal volume of ethyl ether. Here, too, only one solid phase appeared although the temperature was lowered from the initial freezing point (about $-85°$ C) to about $-135°$ C.[13] The formation of only one solid phase clearly showed that the fraction was no eutectic mixture.

Additional evidence concerning the composition of the material was obtained by determining its empirical formula. As a result of 3 determinations, the mean ratio, moles H_2O/moles CO_2, was found by the procedure given by Rossini[14] to be 0.9967 ± 0.0006 as compared with the calculated value, 1.1111 for a nonane C_9H_{20}, and 1.0000 for a nonanaphthene C_9H_{18}. Since all unsaturated and aromatic hydrocarbons, as well as solvent dichlorodifluoromethane, had been carefully removed from the sample, the ratio found by experiment indicates that any impurity present must be polycyclic rather than paraffinic in nature. The molecular weight, found by the lowering in freezing point of cyclohexane, was 126.3 ± 1.0 in good agreement with the calculated value of 126.15 for C_9H_{18}. From these values it is clear that the major constituent is a nonanaphthene or a mixture of nonanaphthenes.

When the results of the various tests are considered together, along with the fact that the material was isolated by fractional crystallization, there is a strong likelihood that the fraction of petroleum is chiefly a single substance. There is, however, a remote possibility that the fraction might be a mixture of isomers which on freezing forms a solid solution having substantially a constant freezing point.

2. PHYSICAL PROPERTIES

In table 4 are listed the physical constants of the sample whose freezing curve is shown in figure 3. It had the highest melting point of any fraction resulting from crystallization.

[12] We are indebted to C. P. Saylor of this Bureau for the examination.

[13] In this connection it was found that on cooling an ether solution of a sample of the naphthene having a freezing range of 0.5° C and freezing initially 1° lower than the fraction described in this paper, a second solid phase did appear at a temperature where ether crystals could not possibly be coming out. This second solid phase may have contained another component, but it is equally possible, in this case, that it represented a second crystalline modification of the same component.

[14] BS J.Research 8, 121 (1932) RP405.

TABLE 4.—*The physical constants of a nonanaphthene from Oklahoma petroleum*

Normal boiling point	Freezing point	Specific gravity d_4^{20}	Refractive index n_D^{25}	Heat of fusion	cst in aniline
°C [a] 136.65 ±.05	°C [b] −65.80 ±.05	[c] 0.77883 ±.00002	[d] 1.42730 ±.00005 $dn/dt = -.00045$	K cal/mol [e] 2.79 ±.06	°C [f] 57.0 ±.5

[a] Determined with a Cottrell boiler.
[b] Temperature at which last crystals disappeared on melting.
[c] Determined by the Division of Weights and Measures of this Bureau.
[d] Determined with an Abbé refractometer (Valentine design).
[e] Determined by F. D. Rossini. See BS J.Research **11**, 553 (1933) RP607.
[f] Determined by R. T. Leslie. J.Research NBS **13**, 589 (1934) RP728.

The infrared absorption spectrum of the nonanaphthene was recorded by U. Liddel of the U. S. Bureau of Chemistry and Soils. The similarity of the absorptive index curve of the naphthene (figs. 4 and 5)

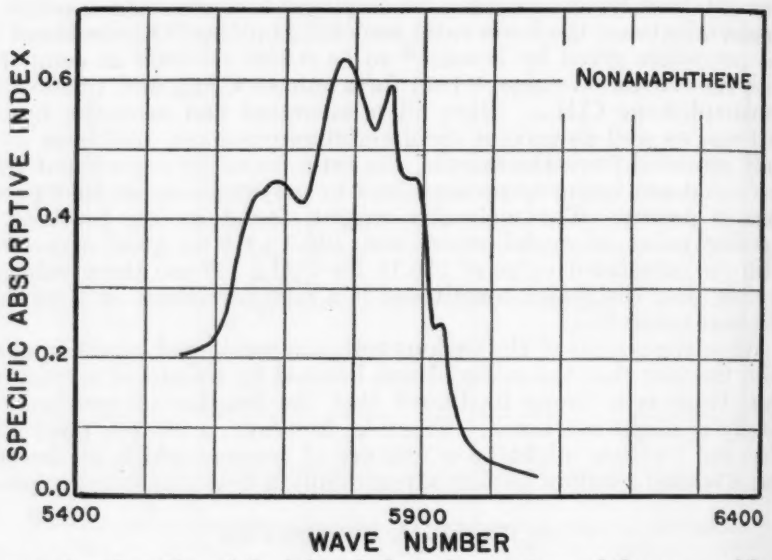

FIGURE 4.—*A portion of the infrared absorption spectrum of the nonanaphthene.*

to those of the hydrocarbon derivatives of cyclopentane [15] is evidence that the compound is a member of the cyclopentane series.

3. CHEMICAL PROPERTIES

Further indication that the compound is a cyclopentane derivative was revealed by its chemical behavior. Zelinsky and coworkers [16] have shown that palladium catalyzes the dehydrogenation of cyclohexane and its derivatives at 350 to 400° C, to form the corresponding aromatic hydrocarbons. The derivatives of cyclopentane, on the contrary, were found to be stable under these conditions. When the vapors of our material were passed repeatedly over palladium asbestos at 350 to 380° C, only a slight evolution of hydrogen occurred. The refractive index of the recovered oil was 1.4305 as compared

[15] Liddel and Kasper, BS J.Research **11**, 599, figure 5 (1933) RP610.
[16] Ber. Deut. Chem. Ges. **45**, 3678 (1912); **56** [B], 1718 (1923).

with 1.4273 for the original. This indicated that very little aromatic hydrocarbon had been produced. Contrary to this behavior, 1,3,-5-trimethylcyclohexane, when treated in a similar manner, was readily dehydrogenated into mesitylene, the corresponding aromatic hydrocarbon.

The result of the attempted dehydrogenation of our nonanaphthene strongly signifies that it is not a cyclohexane derivative. This evidence alone is not conclusive, for it is known that the dehydrogenation test fails to distinguish between a cyclopentane derivative and cyclohexane derivatives containing a *gem* dialkyl group.[17] The latter compounds, containing a completely substituted carbon atom in the ring, cannot be regarded as derivatives of "hexahydrobenzene" because they cannot be dehydrogenated to aromatic hydrocarbons. Zelinsky found this to be the case for 1,1-dimethylcyclohexane.

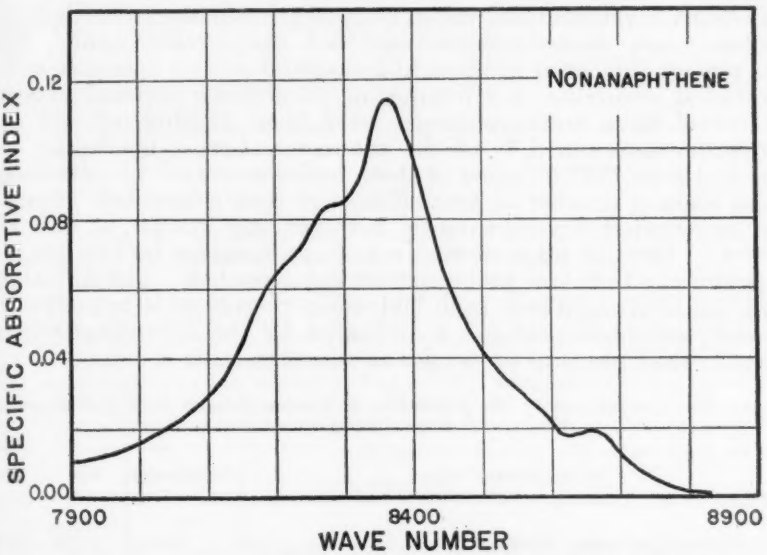

FIGURE 5.—*A portion of the infrared absorption spectrum of the nonanaphthene.*

That our compound is probably no cyclohexane derivative of this type is shown by the fact that all the known nonanaphthenes which are cyclohexanes having a *gem* dialkyl linkage boil at temperatures well above 137° C.

When treated with the nitrating mixture referred to earlier in this paper, the isolated nonanaphthene was oxidized without forming a nitro product. On the contrary, 1,3,5-trimethylcyclohexane, when treated with the same reagent, formed an appreciable amount of a nitro compound. This experiment is also evidence that the petroleum product is not a derivative of cyclohexane.

IV. POSSIBLE IDENTITY OF THE ISOLATED NONANAPHTHENE

Markownikoff and Ogloblin detected the presence of a nonanaphthene in a Baku petroleum distillate which boiled at 135 to 136° C.[18]

[17] Ber. Deut. Chem. Ges. **56** [B], 1716 (1923).
[18] Ber. Deut. Chem. Ges. **16** [B], 1873 (1883).

It too would form no nitro-product. The density of the distillate (0.7652 at 20° C) was definitely lower than that of our material, indicating that it was a mixture of naphthene and isononane. The boiling range of their fraction, however, was the same as that for the distillate in which the nonanaphthene of this investigation was first discovered. Zelinsky likewise was able to detect the presence of a nonanaphthene, which could not be dehydrogenated, in the distillation fraction of Baku petroleum boiling between 136 and 137.5° C.[19] Combustion analysis indicated, however, that it also was a mixture of naphthene and isononane.

It is possible that in each case the same nonanaphthene has been encountered. Assured that our compound is a derivative of cyclopentane, one is still confronted with which of the large number of possible cyclopentane derivatives containing nine carbon atoms it might be. The compound must be one of the isomers of the following: tetramethylcyclopentane, methylpropylcyclopentane, dimethylethylcyclopentane, diethylcyclopentane, and butylcyclopentane. When one reflects that most of these hydrocarbons exhibit space, as well as structural isomerism, the number of possibilities becomes amazing. A few of these nonanaphthenes have been synthesized and their properties determined.[20] Of the known members of the family, very few boil near 137° C; most of them boil above 140° C. By boiling point alone a number of possibilities are thus eliminated. Some of the dimethylethylcyclopentanes, however, are known to boil near 137° C. Possibly other derivatives of cyclopentane boil at this temperature also but their properties are not recorded. The probability that the nonanaphthene from Oklahoma petroleum is related to the dimethylethylcyclopentanes is indicated by the approximate agreement in their physical properties as shown in table 5.

TABLE 5.—*Comparison of the properties of nonanaphthene from petroleum with those for 2 dimethylethylcyclopentanes*

Nonanaphthene C_9H_{18}	Boiling point	d_4^{20}	n_D^{25}
	°C		
From Oklahoma petroleum. White and Rose	136. 65	0. 7788	1. 4274
1, 4-dimethyl-2-ethylcyclopentane. Zelinsky and Pappe, J. Russ. Phys. Chem. Soc. **37**, 627(1905)	135.5 to 137	. 7700	1. 4213
1, 3-dimethyl-2-ethylcyclopentane. Zelinsky and Glinka, J. Russ. Phys. Chem. Soc. **39**, 1170(1907)	135 to 137	. 7703	----------

V. CONCLUSION

The complete identification of the nonanaphthene must await further investigation. Even if its structural formula could be established, the question as to which stereoisomer (cis or trans) it was, would still require answering. The determination of the amount of this hydrocarbon in Oklahoma petroleum must also be postponed until a study of the naphthene fraction boiling immediately above it is completed. From the four liters of mixture which distilled over between 136.8 and 137° C it is safe to say that the crude oil contains not more than 0.1 percent of the nonanaphthene boiling at 136.65° C.

We wish at this time to acknowledge gratefully the advice of the late Dr. E. W. Washburn, who, before his death, directed this research.

WASHINGTON, August 16, 1934.

[19] Ber. Deut. Chem. Ges. **56** [B], 1718 (1923).
[20] Beilstein's Handbuch, 4th ed., Ergänzungswerk, **V**, 18–19.

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INVESTIGATION OF COMMERCIAL MASONRY CEMENTS

By Jesse S. Rogers and Raymond L. Blaine

ABSTRACT

Information on the properties of masonry cements being very meager, or at least, in general, not comparable, the investigation reported here was initiated. Forty-one commercial masonry cements were studied with respect to chemical composition, fineness, weight per unit volume, volumetric flow of the neat pastes, and bulk specific gravity, while mortars made from those cements were studied with respect to resistance to deformation, water-retaining capacity, volume, yield, linear changes, compressive and transverse strength, efflorescence, durability when subjected to cycles of freezing and thawing, and absorption.

It was found that the cements could be classified as hydraulic limes, hydrated limes, natural cements, blast-furnace-slag cements containing various additions, several cements whose composition could not be positively determined, or portland cements with and without admixtures, the quantities of which varied from small amounts to amounts larger than the quantity of portland cement. About half of those studied contained water-repellent additions.

The physical properties of the mortars made from the cements also varied over a wide range. For example, the weight per cu. ft. of cements varied from 39.7 to 89.9 lb. The compressive strength of the mortars when tested at 28 days ranged from 50 to 3,650 lb/in.^{2} The addition of water-repellent material strikingly affected the properties of mortars made from cements to which such additions had been made. The workability particularly seemed to be increased, due to the incorporation of air in the mortar during mixing, brought about by the water-repellent additions acting as emulsifying agents.

A discussion of the essentials of a specification for masonry cement is presented.

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I. INTRODUCTION

Information on the properties of many of the cements used principally in masonry being either very meager or, in general, not comparable, the present investigation was initiated. Forty-one such cements were collected from manufacturers and studied according to the outline under sections II, III, and IV of the table of contents.

II. THE CEMENTS

1. CHEMICAL COMPOSITION

The chemical analyses are presented in table 1. These cements may be classified as hydraulic or hydrated limes (indicated in the table as HL), natural cements (N), portland cements or portland cement with small quantities of admixtures (P), portland cements with the addition of hydrated lime (PL), portland cement mixed with various unidentified materials (PM), blast furnace slags with various additions (S), and 2 whose identity could not be established (U).

Water-repellent materials were present in about half of the cements as shown in table 1. These materials were apparently added to the cements for increasing either or both the water-repellent or plastic properties of mortars made from them. The amount of material identified as a petroleum product varied from 0.2 to 0.5 percent; that as fatty acid with three exceptions was less than 0.10 percent. The 3 exceptions contained 0.14, 0.22, and 0.48 percent. Numbers 34 and 39 contained water-repellent materials, but in such small quantities that they could not be identified.

The "free lime" determination as carried out by the ammonium acetate method, shows that not only CaO but $Ca(OH)_2$ serves in a way to indicate in certain cases the amount of hydrated lime added. Large proportions of "insoluble" in some of the portland cements suggest that siliceous material was added to improve some of the desirable characteristics, such as workability, water retention, etc. A high ignition loss with low "free lime" indicates the use of limestone dust as a plasticizing agent.

TABLE 1.—*General nature, analyses, fineness, and weights per cubic foot of the cements*

Identification number	General nature [a]	SiO_2	Fe_2O_3	Al_2O_3	CaO	M_gO	SO_3	Ignition loss	Insoluble	"Free lime"	Lb/ft³ rodded	Lb/ft³ loose	Percent retained 325 sieve	Percent retained 450 sieve	Water repellent additions [b]
1	PN	22.1	1.8	8.1	33.5	20.6	0.04	13.9	1.6	13.3	62.2	56.0	17.7	28.3	a
2	PL	12.5	1.2	4.3	59.3	1.0	0.6	20.8	7.0	19.9	56.5	49.9	------	------	e
3	HL	17.3	1.6	6.7	58.9	1.8	0.5	12.6	1.3	19.2	50.3	42.1	11.0	20.0	e
4	S	32.2	0.8	11.3	49.5	2.0	2.1	2.3	0.7	10.9	66.4	54.6	8.1	35.3	e
5	PL	12.8	1.9	4.3	56.4	14.6	1.2	8.2	0.2	21.1	47.7	38.5	------	------	e
6	PM	28.6	7.8	7.4	44.8	3.4	1.2	8.4	16.8	0.2	73.1	64.6	------	------	e
7	N	24.4	2.6	6.3	36.0	21.2	1.9	7.8	10.8	1.7	63.0	55.0	15.3	20.5	b
8	PM	24.7	3.0	7.1	59.3	0.8	3.7	1.4	0.2	1.0	72.0	63.4	13.2	23.4	a
9	PM	19.5	2.5	6.9	48.7	1.2	1.2	20.1	4.7	0.8	67.7	59.5	18.1	33.0	e
10	PM	15.5	1.8	3.3	56.9	4.4	1.1	16.9	2.8	4.5	70.3	61.4	17.3	29.2	b
11	N	24.1	1.2	9.7	34.5	22.6	3.0	4.7	10.8	0.9	59.0	51.7	10.4	22.1	b
12	N	24.7	3.5	5.8	49.8	6.3	1.6	7.5	10.5	4.5	65.1	55.8	23.2	38.1	e
13	N	20.6	2.5	5.1	36.2	23.9	2.3	6.4	7.5	5.0	56.2	47.5	10.4	21.0	b
14	PM	12.1	0.5	3.1	61.2	3.3	1.3	18.6	0.3	13.0	63.4	55.6	11.2	20.4	b
15	S	33.0	0.9	9.7	49.9	2.0	2.7	1.8	3.2	6.2	71.7	63.1	17.3	37.2	b
16	PN	19.5	2.4	7.8	52.7	2.7	1.7	12.5	5.9	11.0	61.2	55.2	5.3	11.3	b
17	PL	7.7	1.4	2.5	53.3	20.8	0.7	13.6	0.3	27.5	43.4	38.2	23.1	28.2	e
18	P	21.8	0.4	1.3	71.4	1.8	0.7	2.8	0.4	16.7	64.7	55.8	9.2	31.3	e
19	P	24.2	0.4	4.7	65.3	1.4	1.9	2.4	0.3	0.2	87.7	80.3	10.3	25.4	b
20	P	21.9	0.5	5.8	63.0	4.4	1.9	2.7	0.5	3.1	89.9	80.6	26.2	46.2	b
21	PL	11.5	1.8	3.0	66.4	4.1	0.2	13.1	0.6	29.3	41.8	34.8	9.1	20.3	e
22	PM	13.5	1.8	4.4	52.5	11.8	1.2	14.7	5.6	10.7	59.2	51.6	21.0	27.4	e
23	S	34.2	2.0	10.7	46.7	2.9	0.1	2.9	0.6	6.2	66.9	61.1	12.4	32.1	e
24	S	32.2	2.3	9.9	43.5	5.2	3.6	2.9	8.4	0.5	65.3	57.2	5.4	17.1	b
25	PL	8.9	1.6	3.5	53.1	9.6	0.9	22.6	0.9	7.4	63.5	57.2	20.4	33.5	a
26	PL	10.3	1.5	2.8	51.2	21.3	1.3	12.3	4.3	27.5	49.4	43.8	20.3	34.2	e
27	S	38.6	3.4	14.2	33.3	2.5	1.0	5.2	39.7	0.5	69.7	61.8	27.2	40.3	e
28	P	20.8	2.8	5.5	62.4	2.3	1.5	5.0	1.1	1.7	72.9	66.0	14.2	29.3	a
29	U	25.5	5.0	10.4	46.5	2.6	0.4	9.2	2.7	9.5	63.2	57.3	43.3	49.7	e
30	PL	8.6	1.1	3.6	53.3	21.7	1.1	11.7	0.9	28.3	45.4	39.8	13.1	28.0	e
31	P	21.2	2.8	5.7	63.3	2.3	1.5	2.5	0.8	1.8	79.1	70.2	19.0	34.1	a
32	PM	14.6	1.8	3.9	64.5	1.7	1.3	12.0	0.9	18.3	63.0	56.5	18.2	28.1	e
33	S	28.3	0.6	7.3	45.6	13.1	3.3	2.1	0.5	4.6	66.3	58.0	5.3	23.0	b
34	PL	12.8	1.4	3.4	66.6	3.2	1.1	11.3	0.2	32.8	57.2	50.4	40.3	45.3	d
35	PM	16.7	1.8	3.7	57.1	5.1	1.4	14.1	0.3	0.6	71.2	64.4	18.2	33.5	a
36	PM	14.1	2.3	5.1	57.1	1.4	0.2	19.6	0.1	0.8	65.1	56.5	4.3	16.2	c
37	HL	7.6	1.0	2.5	70.9	0.5	0.5	17.4	0.2	51.6	39.7	32.5	10.3	20.0	e
38	PM	16.9	1.5	5.4	36.5	26.2	0.7	12.4	8.9	9.0	86.3	76.3	11.3	27.2	b
39	U	23.7	2.2	6.0	59.0	5.1	1.7	1.7	5.6	0.7	62.2	55.5	16.4	24.0	d
40	P	21.1	2.8	5.4	62.4	2.3	1.3	4.5	1.4	2.7	73.0	65.0	13.1	32.2	a
41	P	21.8	2.4	5.7	64.4	1.3	1.7	2.4	0.2	0.7	78.3	67.5	12.0	27.1	a

[a] General nature:
P=Largely portland cement;
PL=Portland cement and hydrated lime mixtures;
PM=Portland cement mixed with unidentified material;
PN=Portland cement and natural cement mixtures;
N=Natural cement;
S=Large amounts of slag;
U=Not identified;
HL=Hydraulic or hydrated lime;

[b] Water repellent additions:
a=petroleum product
b=fatty acid derivative
c=rosin
d=unknown
e=not detected

2. FINENESS

The fineness (table 1)[1] was determined by wet screening with kerosene each cement through a no. 325 and a no. 450 sieve. The latter screen was made by chromium plating a no. 325 sieve until the openings were such that they would pass a particle less than 50 microns in diameter. The no. 325 sieve passes a 60-micron particle. The data indicate that with two exceptions the desirable fineness was realized.

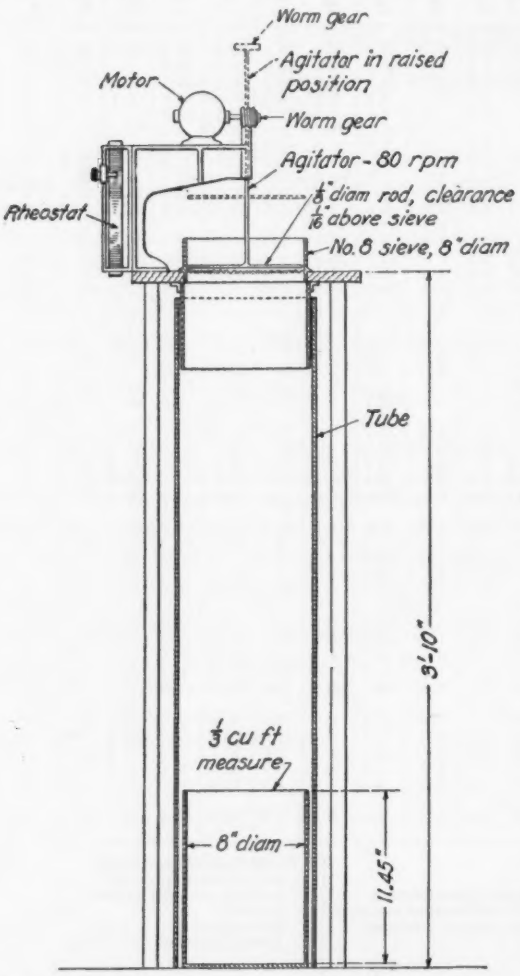

FIGURE 1.—*Apparatus for determining weight per unit volume of cement.*

3. WEIGHT PER UNIT VOLUME

The weight of each cement was determined as received, that is, without drying, sifting, or other preliminary preparation. The weight per volume of compacted cement was determined by rodding the cement with a ⅝-in. steel rod with a bullet-shaped end. The cement was rodded, in 3 layers, into a ⅓-cu. ft. aluminum measure. The excess cement was struck off with a straight edge. The weight per volume of loose cement was determined by use of the device shown in figure 1. The cement was shaken on a sieve, a small quantity at a time, with the agitator continually revolving, until the measure was heaping full. The excess was struck off with a straight edge. In either procedure, the measure was filled and weighed repeatedly until the results checked to the nearest 10 g. There was a decrease in weight per unit volume with succeeding determinations for the first 2 to 5 trials.

The rodded weight varied from 39.7 to 89.9 lb/cu ft (table 1), the mean being 64.7. The loose weight varied from 32.5 to 80.6 lb/cu ft, the mean being 56.3. Those cements that contained large propor-

[1] The supply of cements nos. 2 and 5 was exhausted prior to these measurements. Cement no. 6 was compounded in the laboratory. Sieve analysis of this cement would therefore not be comparable with the others.

tions of portland cement had the higher weights per cu ft. However, mixtures of portland cement with large proportions of hydrated lime were among those of lightest weight, e. g., cements nos. 5, 17, and 26.

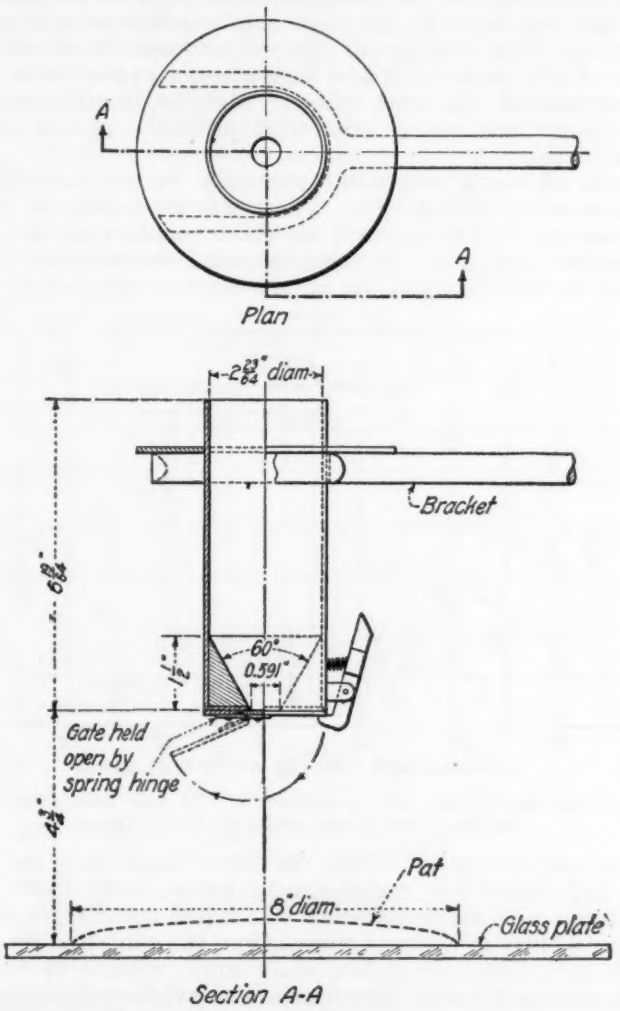

FIGURE 2.—*Device for determining volumetric flow of neat cement pastes.*

III. CEMENT-WATER PASTES

1. VOLUMETRIC FLOW AND SPREAD

The apparatus used to measure the volumetric flow and spread, shown in figure 2, was developed by committee C–1, cement, American Society for Testing Materials, for a study of a method to determine the normal consistency of portland-cement pastes.

The tests made with neat pastes (cement and water) included determination of the amounts of mixing water required to give a spread of 8 in., the time of flow of pastes and the bulk specific gravity of the pastes.

Cement and water were vigorously mixed for 5 min in a metal vessel with a metal stirrer. The container of the apparatus was then immediately filled level with the top. The time required for the paste to flow out of the container, from the time of springing the catch to the first break in the stream of paste, was measured with a stopwatch. The average of the measurements across several diameters of the paste as it had been allowed to flow onto the glass plate was termed the neat spread. Batches of different proportions of cement and water were tried until the spread was 8 in. within ±0.1 in.

The ratio of water to cement necessary to produce this spread ranged between 0.36 and 1.00. There was no consistent difference in water-cement ratios required for the cements with and without water-repellent additions. Further, no consistent relation was found between either the composition or the fineness of the cements and

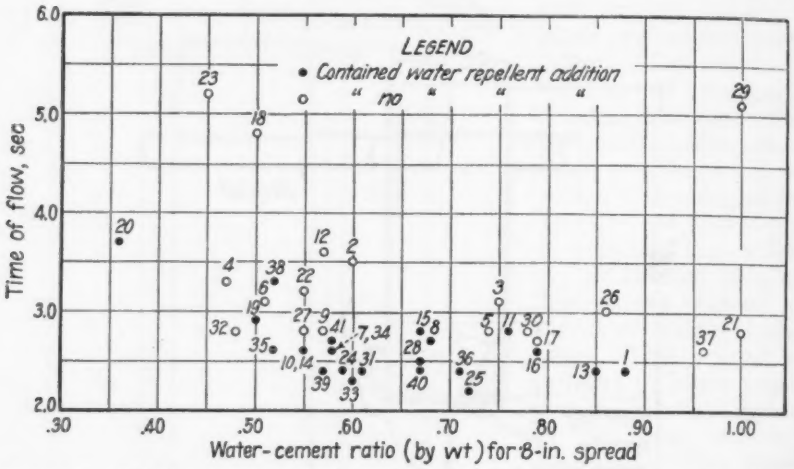

FIGURE 3.—*Relation between time of volumetric flow and water-cement ratio (by weight) of neat pastes giving an 8-inch spread.*

their water requirements. While the pastes made from the portland cements had rather low water-cement ratios, there were portland-cement blends with other materials which had equally low ratios.

The time of flow of the neat pastes from the container ranged from 2.2 to 5.2 sec. The time of flow of an equal volume of water from the container was 2.0 sec. The maximum deviation of any individual determination from the average of 3 was 0.2 sec. Figure 3 shows that generally the pastes made from cements containing water-repellent additions had a lesser time of flow.

2. BULK SPECIFIC GRAVITY

Neat pastes were prepared by mixing for 5 min cement with the amount of water required for an 8 in. spread. Immediately after mixing, the paste was poured into a 200 ml erlenmeyer flask with a top ground and fitted with a ground glass cover plate. The excess paste was struck off with the cover, and the outside of the flask wiped clean. The covered flask and contents were weighed to the nearest 0.1 g, and the bulk specific gravity of the paste was computed from the known volume of the flask and the net weight of the paste.

The bulk specific gravity of the neat pastes varied from 0.83 to 1.93 as shown in figure 4. The plotted points in this figure are in 2 groups. One contains 16 of the 23 cements which had water-repellent additions; the other, all the non-water-repellent cements and also the 7 cements not contained in the first group. The great differences in bulk specific gravities of the neat pastes were caused mainly by the retention of different amounts of air incorporated during the mixing. The various proportions and specific gravities of the component materials were also factors of moment. It was evident that during the mixing of the pastes those containing water-repellent additions readily incorporated air. No direct determination of the amounts of air present in each case was made. An indication of the air incorporated was obtained from the total volumes of dry rodded cement plus water used to produce 1 volume of the neat paste. The computed sum of the entering materials varied from 0.83 to 2.00 times the actual volume of paste produced and was less than 1.00 for 10 of the cements, which proved that these pastes contained air. The water-cement ratio of the neat pastes is shown in the last column of table 2.

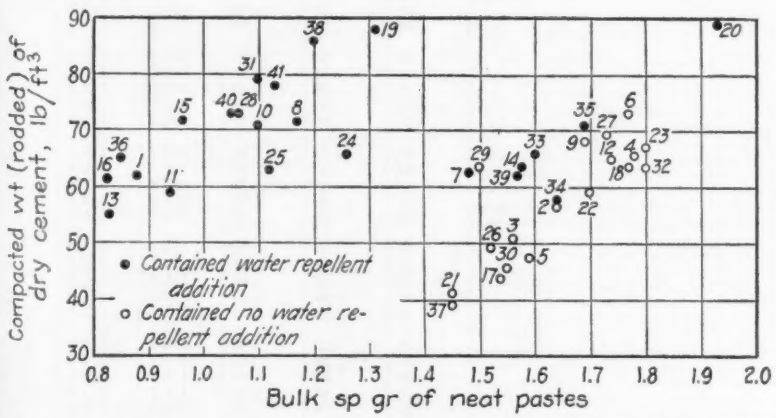
Compacted wt (rodded) of dry cement, lb/ft3
Bulk sp gr of neat pastes
• Contained water repellent addition
o Contained no water repellent addition

FIGURE 4.—*Relation between weight per cubic foot of cement (compacted) and bulk specific gravity of neat pastes.*

IV. MORTARS

1. FRESH MORTAR

The compositions of the mortars were as follows:

Mortar X.—One part of cement, 3 parts of standard Ottawa sand, by weight. In the stirring resistance tests and in the measurements of the water-retaining capacity, the amount of water was varied by increments of 1 percent of the weight of the dry materials. For the measurement of length change and for determining the compressive strength, 3 different amounts of water were used, namely, that to produce normal flow,[2] 1 percent more and 1 percent less. The amount of water required for normal flow was used in preparing specimens for the measurements of transverse strength, absorption, durability, and for the study of efflorescence.

[2] Normal flow is a flow of 100 to 115 obtained upon a 10-in. flow table using 25 one-half in. drops. See Federal specification SS–C–181 for masonry cements, or Proc. ASTM. 32, pt. I, 698 (1932).

TABLE 2.—*Composition of mortars*

Cement number	Water-cement and cement-sand ratios					
	Water-cement ratio by weight at normal flow			Cement-sand ratio by weight		Water-cement ratio by weight in paste, mortar Z
	Mortar X	Mortar X–1	Mortar Y	Mortar Y	Mortar Z	
1	[a] 0.72	[b] 0.68	[c] 0.90	[c] 1:5.2	[c] 1:5.8	0.88
2	.68	.64			1:2.6	.60
3	.72	.68	1.20	1:6.4	1:3.1	.75
4	.60	.52	.77	1:4.9	1:2.3	.47
5	.76	.72	1.20	1:6.8	1:3.0	.74
6	.64	.64	.79	1:4.4	1:2.3	.51
7	.64	.60	.72	1:5.1	1:2.9	.58
8	.64	.64	.81	1:4.5	1:3.9	.68
9	.72	.68	.86	1:4.8	1:2.5	.57
10	.54	.52	.64	1:4.6	1:4.0	.55
11	.68	.68	.80	1:5.5	1:5.1	.76
12	.64	.60	.91	1:5.1	1:2.5	.57
13	.68	.68	.85	1:5.8	1:6.1	.85
14	.56	.56	.80	1:5.1	1:2.7	.55
15	.60	.56	.78	1:4.5	1:4.7	.67
16	.56	.54	.75	1:5.3	1:4.4	.79
17	.76	.76	1.49	1:7.5	1:3.2	.79
18	.56	.56	.80	1:5.0	1:2.3	.50
19	.54	.48	.60	1:3.7	1:3.1	.50
20	.54	.52	.59	1:3.6	1:1.9	36
21	.88	.88	1.50	1:7.7	1:3.8	1.00
22	.64	.60	.95	1:5.5	1:3.5	.55
23	.56	.54	.77	1:4.8	1:2.2	.45
24	.56	.56	.66	1:5.0	1:3.4	.59
25	.60	.60	.78	1:5.1	1:4.2	.72
26	.80	.80	1.37	1:6.5	1:3.3	.86
27	.68	.64	.85	1:4.6	1:2.4	.55
28	.56	.52	.66	1:4.4	1:4.3	.67
29	1.04	1.00	1.33	1:5.1	1:3.6	1.00
30	.76	.70	1.29	1:7.1	1:3.1	.78
31	.52	.52	.60	1:4.1	1:4.0	.61
32	.60	.56	.89	1:5.1	1:2.2	.48
33	.56	.50	.68	1:4.9	1:2.7	.60
34	.68	.64	1.06	1:5.7	1:2.6	.58
35	.56	.56	.70	1:4.5	1:2.5	.52
36	.56	.50	.63	1:5.0	1:5.5	.71
37	.76	.76	1.52	1:8.2	1:3.6	.96
38	.48	.48	.52	1:3.7	1:3.5	.52
39	.56	.56	.73	1:5.2	1:2.7	.57
40	.56	.52	.65	1:4.4	1:4.3	.67
41	.52	.52	.58	1:4.1	1:3.8	.58

[a] Mortar X=1:3, by weight cement, standard sand mortar.
[b] Mortar X–1=1:3 by volume cement mixed sand mortar (see text).
[c] Mixed sand used in mortars Y and Z.

Mortar X–1.—One part of cement, 3 parts of mixed sand, by weight. The mixed sand was composed of 2 parts by weight standard Ottawa sand and 1 part pit-run Ottawa sand. The fineness modulus was 2.62. Three different amounts of water were used, namely, that which produced normal flow, 1 percent more, and 1 percent less. This mortar was used in compressive tests only.

Mortar Y.—One part of cement and 3 parts of the above-described mixed sand by dry-rodded volumes. Enough water was added to this mortar to produce normal flow. The proportions of sand, cement, and water by weight are given in table 2. This mortar was studied with all the tests except linear changes during hardening.

Mortar Z.—One volume neat cement paste to 1.57 volumes of the dry-rodded mixed sand,[3] the water content of the paste being that required to give a spread of 8 in. plus or minus 0.1 in. in the neat spread test. The proportions by weight are given in table 2. Mortar Z was tested for strength in compression only.

(a) PREPARATION OF MORTARS

For mortars X, X–1, and Y, the sand and cement were mixed to a uniform color in a metallic vessel. Water was then added and the

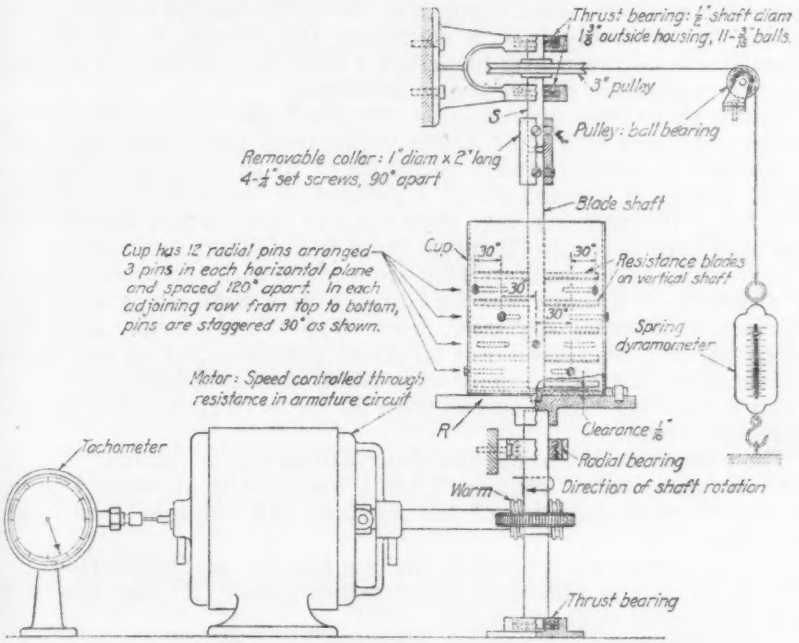
Thrust bearing: ½" shaft diam
1⅜" outside housing, 11-⅜" balls
3" pulley
S
Pulley: ball bearing
Removable collar: 1" diam x 2" long
4-¼" set screws, 90° apart
Blade shaft
Cup has 12 radial pins arranged 3 pins in each horizontal plane and spaced 120° apart. In each adjoining row from top to bottom, pins are staggered 30° as shown.
Cup
30°
Resistance blades on vertical shaft
Spring dynamometer
Motor: Speed controlled through resistance in armature circuit
R
Clearance 1/16"
Radial bearing
Direction of shaft rotation
Tachometer
Worm
Thrust bearing

FIGURE 5.—*Device for measuring resistance of mortars to stirring.*

mixing continued for 5 min. The mortars were then allowed to stand for 14½ min., when they were again stirred for one-half min. This procedure was followed in order to incorporate the ingredients into a homogeneous mass, for in some, segregation resulted on standing. For mortar Z the paste was weighed into the metallic vessel and the weight equivalent of 1.57 volumes of mixed sand added and the mixing continued for 5 min. It was allowed to stand for 14½ min, and again mixed for one-half min. Many of the cements, particularly those containing integral water-repellent agents or plasticizers, showed a marked resistance to wetting, particularly during the first 2 or 3 min. Fourteen and one-half min was assumed adequate as a soaking period.

(b) STIRRING RESISTANCE AND FLOW

The device shown in figure 5 was used to determine the relative "workability" (stirring resistance) of the mortars. As the apparatus

[3] Usually mortars are proportioned by fixing the ratio of cementing material to sand, the consistency being controlled by the amount of water added. In contrast to this, mortar Z was proportioned by fixing the ratio of the volume of the pastes to the volume of the sand. Preliminary tests indicated that the mortars with few exceptions would have the desired normal flow of 100 to 115 percent when this ratio was 1:1.57.

was first constructed there were no projections attached to the inside of the cup. Observations showed that the mortar slipped on the interior surfaces of the cup, indicating that the resistance was a measure largely of the friction of the mortar on metal. This was particularly noticeable in the stiffer mixes. As it seemed that the working properties of mortars are more a function of resistance to deformation than of resistance to sliding on a metal surface, the apparatus was changed to its present form. Although the blades and projections caused the mortars to deform when the cup was rotated, there may yet have been some slippage at the metal-mortar interface. In this device a revolving cup contained the mortar, in which were inserted several horizontal blades on a shaft connected with a spring balance to measure the resistance developed.

In this part of the investigation mortars X and Y were used. The amount of water in mortar X was varied from that which was found to produce a resistance of about 1,200 g to that which resulted in about 200 g by increments of 1 percent of the weight of the dry material. If less water were used some of the mortars formed balls and gave erratic results; if more, there was distinct segregation.

A great many preliminary tests were made with the present device in which the resistance was measured over a wide range of speeds. Mortars, neat pastes, dry sand, fine lead shot, and a few enamel slips were used in these tests. For all these, the resistance at low speeds decreased rapidly as the speed of rotation increased from one-half to about 5 rpm; for higher speeds from 20 up to 70 rpm, the resistance increased moderately.

The procedure in making the observations was as follows:

1. A mortar batch weighing 1,350 g was used in all cases. Owing to the different densities of the mortars, the volumes varied considerably.

2. The mortar was placed in the cup and the blades inserted.

3. The cup was placed on the rotating platen (R) and the blade shaft connected to the shaft (S).

4. The cup was then rotated at 25 rpm for 5 min.

(a) The load on the balance was then noted at the end of the 5-min. period.

(b) The speed was next increased to 50 rpm. The load was then noted after 1 min. at this speed.

(c) The speed was then further increased to 70 rpm and the load again noted at the end of 1 min at this speed.

The measurements indicated in 4 (a), (b), and (c) were repeated, and then again repeated with the exception that 4 (a) was read at the end of 1 min instead of 5 min for the second and third set of readings.

The three speeds at which the observations were made were used as the result of preliminary tests. These tests indicated that a constant resistance could not be produced under a given set of conditions, at the very low speeds, within a reasonably short time. But it was found on studying the data that for a mortar made of any of the cements, the effect of speed on resistance for any one water-cement ratio between high and low speeds was not as great as the preliminary work indicated. Thus, the average difference for mortar X for all cements for the maximum amount of water used with each cement between the high and low speeds was 60 g. The difference, when

the minimum amount of water was used, was 100 g. Such values are but little beyond the experimental error. Hence the data give the average resistance for the three sets of readings.

The data do not show to what extent stirring resistance was a function of the deformation resistance of the mortars. The observations indicate, however, that surface resistance of the mortar on metal may have contributed a part. With the speeds used, turbulence was observed on the free surface of the mortar which would indicate the same condition within the mortar mass; hence it would be expected that the resistance values were influenced somewhat by the density of the mortars. Nevertheless, the resistance seemed to provide a numerical measure which agreed with the judgment and experience of the operator as to the working properties.

The difference between the amount of water used in the mortars, which resulted in a resistance of 200 g, and that which gave 1,200 g has been termed the "water range of the mortars." This is represented graphically by the lengths of the bars in figure 6. Their lengths and positions in the graph are equally important. A long, bar indicates that the resistance is not as sensitive to changes in the water content as that represented by a short bar. A bar toward the left of the figure indicates that the mortar required less water to produce a workable mix than one to the right. It was observed, while preparing the mortars, that those containing cements having water-repellent additions generally worked more easily than those prepared from the non-water-repellent cements. The added material appeared to act as a plasticizing agent. It can be noted in figure 6 that those mortars which contain water-repellent cement are more to the left of the figure than those without the additions. To produce equal ease of working—resistance values within the same range—in the non-water-repellent mortars it was necessary to use more water.

Figure 7 shows the relation between resistance and water content of a few of the mortars of type X. Graphs representing data for the other mortars of this type would be between the extremes shown here. It was found that the logarithm of the resistance was proportional to both the percentages of mixing water and the percentage spread of the mortar as measured by the flow table. Use was made of these relations in extrapolating values of percentage flow and percentage of mixing water, as shown in figure 6.

Two important facts are demonstrated by these curves: first, that to obtain the same resistance values for different cements in this type mortar, the water requirements varied over a wide range; second, that the resistance values of the mortars of some of the cements change more rapidly than others with equal changes in the mixing water. For example, normal flow of the mortar made from cement 20 gave a resistance of approximately 1,520 g, while with a mortar from cement 1, it gave a resistance of about 350 g. Mortars of the Y type (1:3 mixed sand by volume) showed similar relations. Thus, the mortar from one cement of normal flow gave a resistance of 500 g, whereas the mortar from another cement gave a value of 2,350 g. Apparently, cements which produce "fat" mortars will have lower resistance values at normal flow than those which yield harsh mortars.

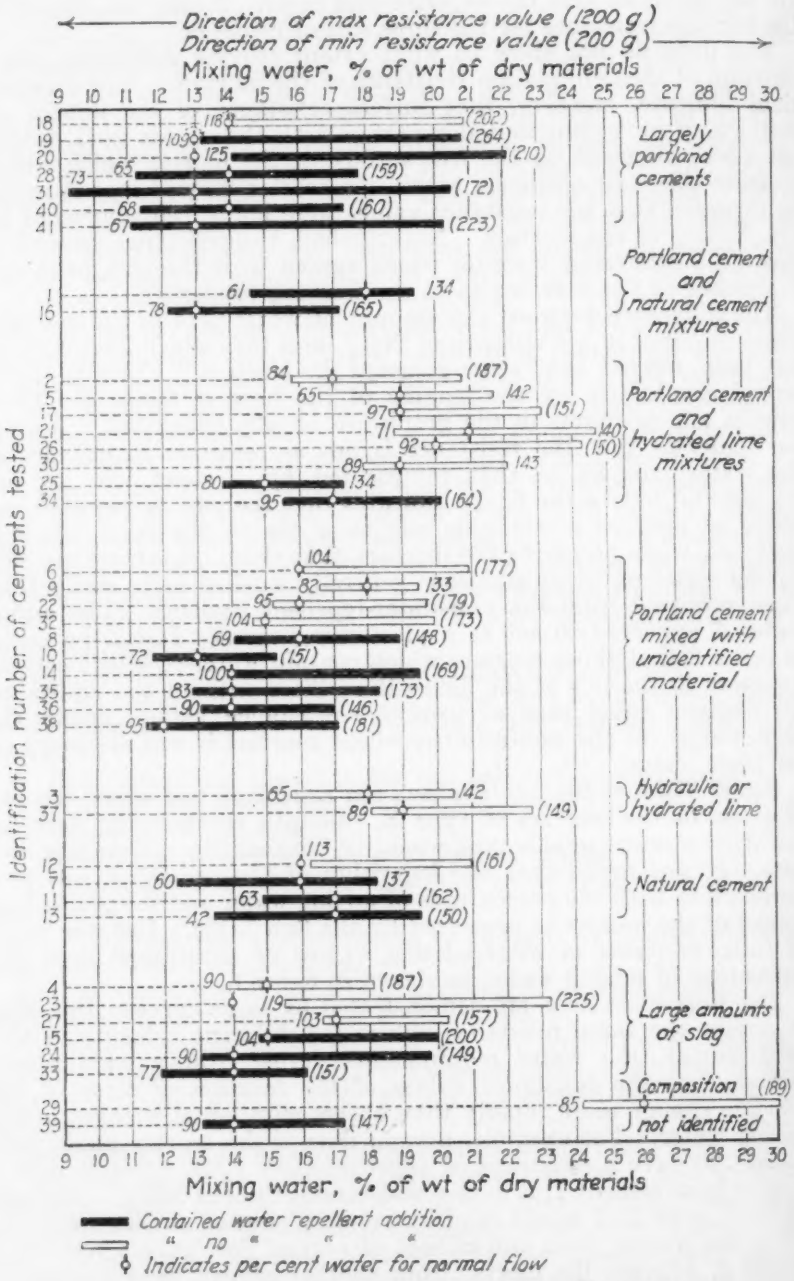
Direction of max resistance value (1200 g)
Direction of min resistance value (200 g)
Mixing water, % of wt of dry materials
9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
Identification number of cements tested
18 19 20 28 31 40 41
1 16
2 5 17 21 26 30 25 34
6 9 22 32 8 16 14 35 36 38
3 37
12 7 11 13
4 23 27 15 24 33
29 39
Largely portland cements
Portland cement and natural cement mixtures
Portland cement and hydrated lime mixtures
Portland cement mixed with unidentified material
Hydraulic or hydrated lime
Natural cement
Large amounts of slag
Composition not identified
Mixing water, % of wt of dry materials
Contained water repellent addition
" no " " "
Indicates per cent water for normal flow

FIGURE 6.—*Water range of cements in type X mortars.*

Extreme resistance values plotted are 200 and 1,200 g. The percent water corresponding to these was obtained by interpolation and extrapolation from graphs plotted from original data.

The numbers at the ends of the bars are percentage increases in spread as measured on the flow table at the corresponding amounts of water; those in parentheses are extrapolated values.

Changes in the flow of mortar X throughout all water-cement ratios found before and after the stirring resistance tests served to classify the cements into three groups. Group 1, in which the final flow was greater than the initial flow, included cements nos. 3, 5, 13, 16, 21, 28, 31, 33, 35, 36, 40, and 41. Group 2, in which the final flow was less than the initial flow, included cements nos. 1, 2, 6, 8, 9, 10, 11, 12, 14, 15, 17, 19, 20, 22, 23, 25, 26, 27, 32, 34, and 37. Group 3, in the low range of water-cement ratios, cements nos. 4, 7, 18, 24, 30, 38, and 39, produced greater initial flow than the final; while with the higher water-cement ratios the initial flow was less

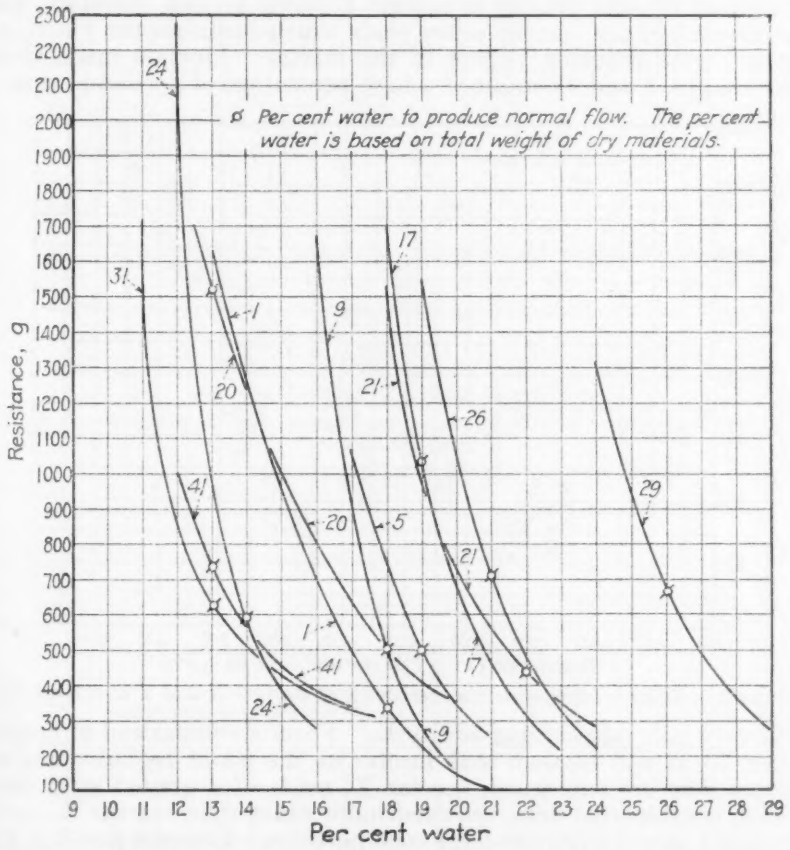

FIGURE 7.—*Variation of stirring resistance with changes in water content, mortar* X.

than the final flow. The converse of this was noted with cement no. 29.

It was observed that group 1 includes cements having water-repellent additions or large proportions of lime. Those in group 2, if containing water-repellent materials, were relatively coarse.

Approximately 16 min had elapsed between the making of the 2 observations, during which time hydration of the cements may have progressed considerably. The hydration would usually be considered as producing a stiffening and therefore reduced flow. But it is conceivable that the early hydration products might be such that

they would confer unctuousness and therefore greater flow to a mortar. It is consequently not surprising that certain of the mortars have developed greater flow during agitation and the lapse of the time required for making the resistance observations.

How the several cements affected the relative resistance of mortar X (1:3 by weight standard sand) and of mortar Y (1:3 by volume mixed sand) is shown in figure 8. Here it is seen that with the exception of the mortars made from cements nos. 19 and 20, the resistance of mortar Y is considerably higher than that of mortar X. The reason for increased resistance is readily seen to be due to the greater proportion of sand present in mortar Y (table 2) and, therefore, the less amount of the cement-water paste which furnishes the plasticizing or "work-reducing" agent in the mortar. Mortars made from cements nos. 6 and 9 contained a high percentage of portland cement

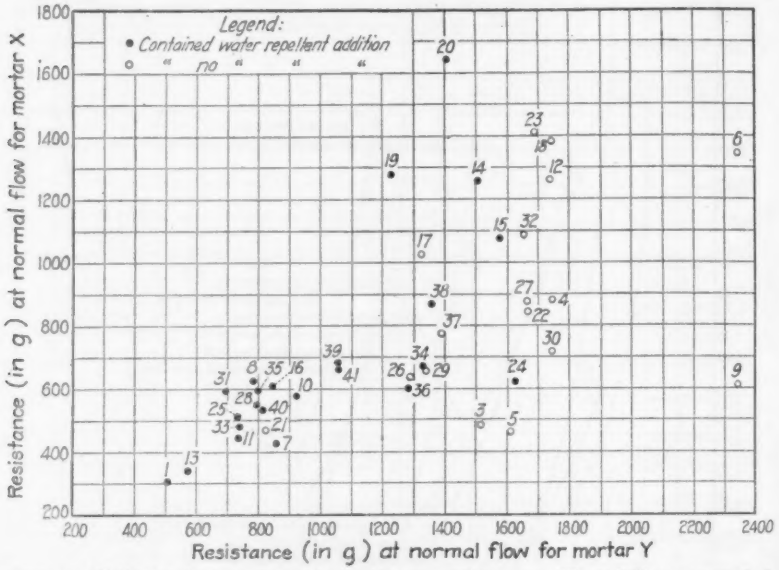

FIGURE 8.—*Relation between stirring resistance of mortars* X *and* Y *at normal flow.*

with very poor plasticizing additions. From a comparison of figures 9 and 10, it will be seen that insofar as the water requirements at normal flow are concerned, mortar Y, made of a graded sand containing considerable fines, required more water than mortar X, composed of 1 size of relatively large sand particles. Cements nos. 3, 5, 17, 21, 26, 29, 30, and 37, which were high in hydrated lime, required more water for the same workability than other cementing materials, and caused the mortar containing them to have high water requirements.

In figures 9 and 10 there have been plotted the resistance values and water-cement ratios of mortars X and Y at normal flow. The mortars have been studied at this consistency largely because of the inclination to accept the normal flow as giving a consistency closely approaching that which would be used in the practical application of the mortars. This inclination is evidenced by the inclusion of the normal flow as a measure of the consistency in both the Federal [4]

[4] Normal flow is a flow of 100 to 115 obtained upon a 10-in. flow table using 25 one-half in. drops. See Federal specification SS-C-181 for masonry cements, or Proc. ASTM 32, pt. I, 698 (1932).

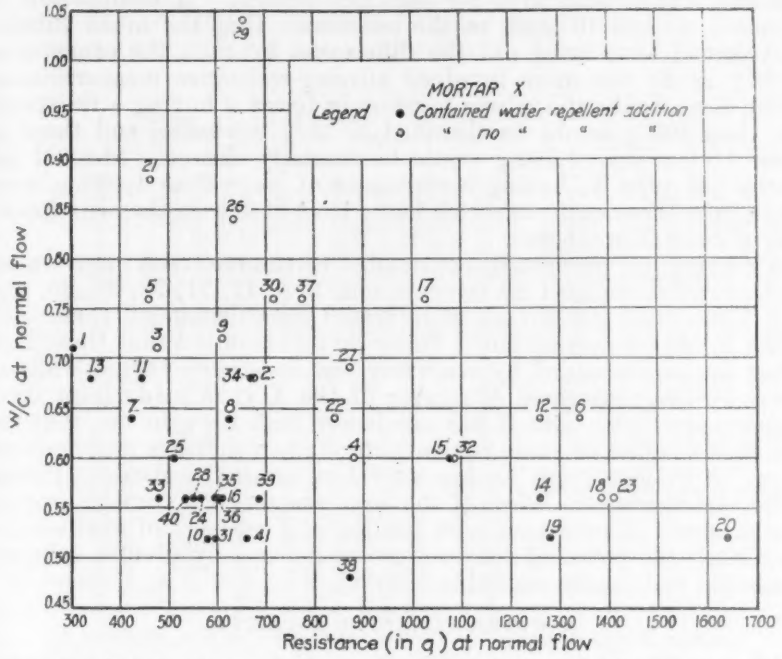

FIGURE 9.—*Relation between water-cement ratio and stirring resistance of mortar* X *at normal flow.*

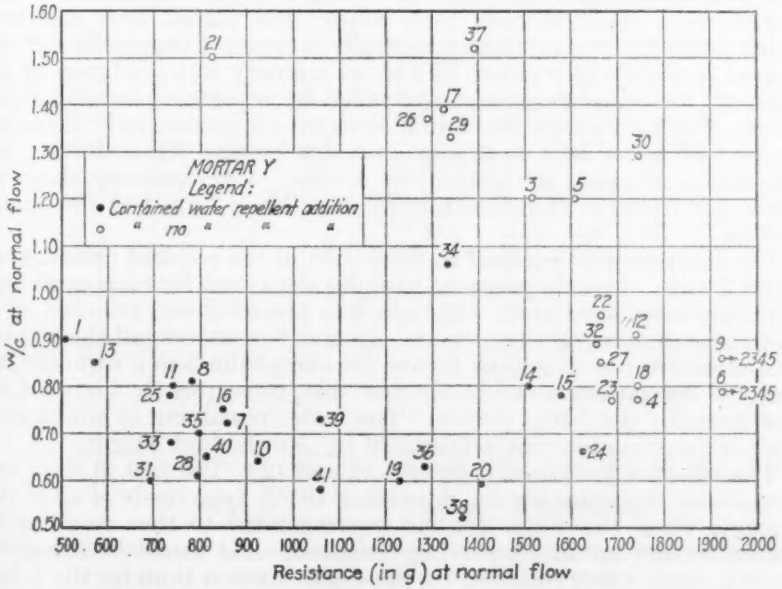

FIGURE 10.—*Relation between water-cement ratio and stirring resistance of mortar* Y *at normal flow.*

and the ASTM standards for masonry cement. A comparison of figures 3, 9, and 10 leads to the conclusion that the much simpler neat spread tests bring out the differences between the cements as readily as do the more involved stirring-resistance measurements. There is no doubt that those mortars in figure 9 having a resistance less than 800 g would be classified as very workable, and those in figure 10 less than 1,400 g would be similarly classed. Most of the mortars of type Y, having a resistance of more than 1,400 g, were made from those cements which had a time of flow in the neat spread test of more than 2.6 sec.

Attention has previously been called to the relatively high water-cement ratios required by cements nos, 3, 5, 17, 21, 26, 29, 30, and 37. Their high percentage of hydrated lime demanded these high ratios to obtain normal flow. In figure 9 it is noted that these high ratios are accompanied by relatively low resistance values, while in figure 10 the resistances of mortar of the Y type made from these cements are high. But it has previously been brought out that the low unit weights of these cements resulted in mortars proportioned on a 1:3 volume basis having very low cement contents. Hence, there can be seen the effect of the large amount of hydrated lime on this property of resistance here studied as a measure of workability. As a class the portland cements are about equally divided between the easily and poorly workable mortars.

(c) WATER RETAINING CAPACITY

Mortars X and Y were used in the tests for water-retaining capacity with the same quantity of water as used in determining the resistance values.

A perforated porcelain dish, containing a weighed quantity of the mortar on a sheet of hard filter paper, was placed over a device which could be evacuated to a carefully controlled degree for certain desired periods.[5] A vacuum of 2 in. of mercury was produced by an ordinary water aspirator and controlled by a mercury-column relief valve. Such a vacuum was found to remove approximately the same amount of water in 1 to 3 min as a dry process brick having an absorption of about 6.5 percent in 3 min. A preliminary study of the water removed from mortars by such brick furnished this information.

The mortars were exposed to the action of the reduced pressure for 1 and 3 min. Freshly prepared samples were used for each exposure; duplicate tests were made and each was preceded and followed by a flow measurement on the mortar. In many instances, all the removable moisture was extracted before the end of the 3-min exposure, so that the mortar crumbled in the flow test, consequently there are no flow data for the 3-min period. The water remaining in the mortar after the evacuation was determined by the residual weight.

The data are presented in figures 11 and 12. The first of these figures shows the ratios for the mortars of the X type made of all of the cements when the water content corresponded to that resulting in maximum and minimum stirring resistance. As would be expected, there is more water removed by the 3-min suction than by the 1, but the ratio between these 2 periods is not constant for all of the mortars.

[5] This device, although developed by one of the authors of this paper, was also used by Palmer and Parsons, and is described in their paper, *Rate of stiffening of mortars on a porous base*, Rock Products, 35, no. 18 (1932).

While generally those cements having a large percentage of material passing the no. 450 sieve showed better water retention than the coarser cements, this did not always follow. Cement 29, the coarsest

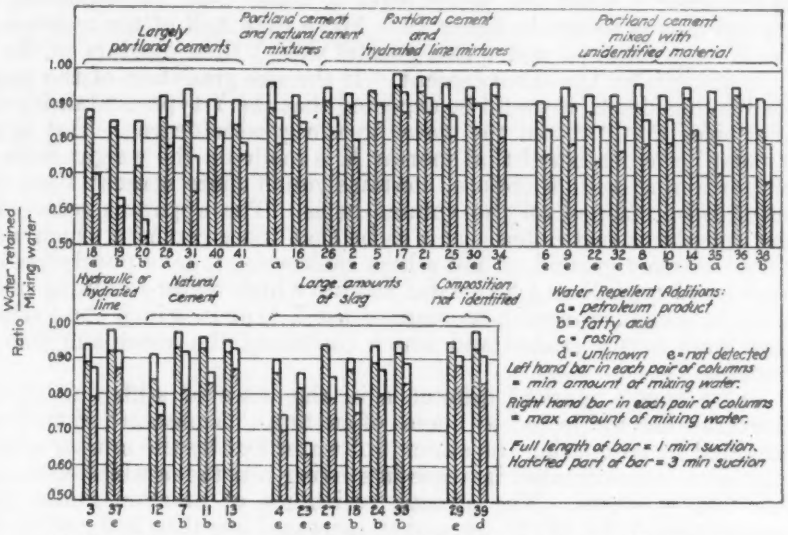
Largely portland cements
Portland cement and natural cement mixtures
Portland cement and hydrated lime mixtures
Portland cement mixed with unidentified material
Ratio Water retained / Mixing water
Hydraulic or hydrated lime
Natural cement
Large amounts of slag
Composition not identified
Water Repellent Additions:
a = petroleum product
b = fatty acid
c = rosin
d = unknown e = not detected
Left hand bar in each pair of columns = min. amount of mixing water.
Right hand bar in each pair of columns = max. amount of mixing water.
Full length of bar = 1 min suction.
Hatched part of bar = 3 min suction

FIGURE 11.—*Water-retaining capacity of cements in type* X *mortar.*

ground cement, had very excellent water retention. Composition seemed to be a dominant feature in controlling this property. Natural cements or cements containing much hydrated lime or partially

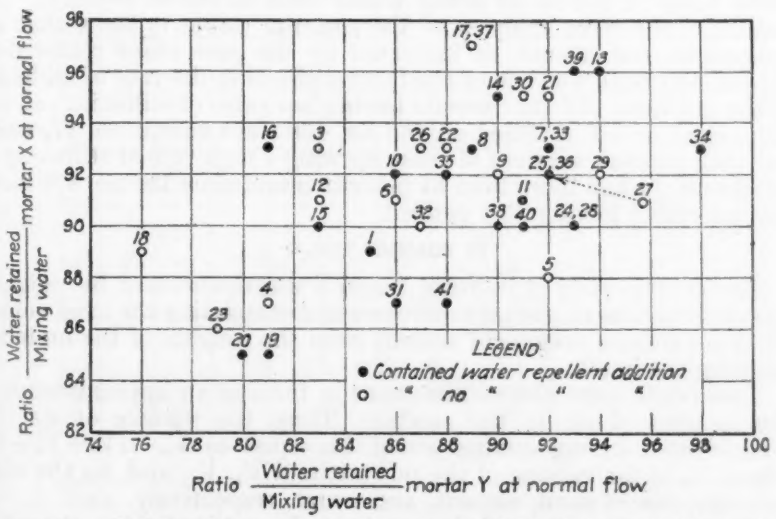
Ratio Water retained / Mixing water mortar X at normal flow
Ratio Water retained / Mixing water mortar Y at normal flow
LEGEND
Contained water repellent addition
no " " "

FIGURE 12.—*Relation between ratios of water retained at the end of one-minute suction to mixing water of mortars* X *and* Y *at normal flow.*

hydrated additions had high water retention. It is not possible to say if these materials are effective only because of their extreme fineness of grind or to their nature being such as to hold tenaciously large

amounts of water. The presence of a water-repellent addition was apparently not effective in reducing the withdrawal of the water.

The relation between the water-retaining properties of mortar X and mortar Y when the percentages of water used corresponded to normal flow is shown in figure 12. More than half of the mortars of the X type retained water to a greater extent than mortars of the Y type made from the same cement. If the size gradation of the sands used is considered, it would be expected that the Y type containing the finer sizes would retain the water to the greater degree. But again it must be remembered that mortar X is made on the weight basis of proportioning and, therefore, contains much more cement than the other, proportioned on the volume basis. The apparent reason for the exceptions just noted seems to be that those cements which were either coarsely ground or had a high bulk weight, gave poorly graded mortars of type X and hence did not have high water-retaining properties in comparison with mortars of the Y type in which the particle sizes were better graded and which contained the lesser amounts of cement.

There was a marked difference in the rates of stiffening of the mortars when subjected to 1 min. of suction. A measure of this was obtained by comparing the amount of water lost by the mortar after 1 min. with the estimated increase in stirring resistance which attended this loss of water. The stirring resistance of mortars made with cements nos. 7, 13, 17, 21, 36, and 39 increased less than 200 g when the water content was changed from that required for a resistance of 200 g to that remaining in the mortar after 1 min. suction, whereas the increase for mortars of cements nos. 4, 12, 18, 19, 20, and 23 was more than 900 g. Those of the first group would tend to retain their workability when used in contact with masonry units of rapid absorption while those of the latter group would tend to stiffen rapidly. The results of the sieve analyses of the cements (table 1) show that the fineness of the cement as indicated by the percentage retained on the no. 450 sieve was one of the factors affecting the rate of stiffening of the mortars. Of the cements having low rates of stiffening, all had 24 percent or less retained on the no. 450 sieve except no. 17, which had 28.2 percent, whereas of those showing a high rate of stiffening all except no. 19 had more than 31 percent retained on the no. 450 sieve, this exception having 25.4 percent.

(d) VOLUME YIELD

The volume yield of mortars Y and Z was determined by weighing the same volume of mortar in all cases and calculating the total volume yield per rodded volume of cement from the weights of the materials entering the batch.

These data were also of assistance in making an approximation of the amount of air in the mortar. Thus, the volume of air (V_a) incorporated during mixing would be equal to $V_m-(V_s+V_c+V_w)$ where V_m is the volume of the mortar, and V_s, V_c, and V_w the absolute volumes of sand, cement, and water, respectively.

The yield of mortars of the two types from the various cements is presented in figures 13 and 14. The former also gives the calculated percentage of air by gross volume of the mixture. One volume of cement plus 3 volumes of sand and enough water to give normal flow resulted in yields varying from 3.29 to 4.19. It is clearly seen, however, how much the yields are influenced by the presence of air.

Further, as previously stated, the presence of the water-repellent compounds induced the incorporation of the air during the mixing,

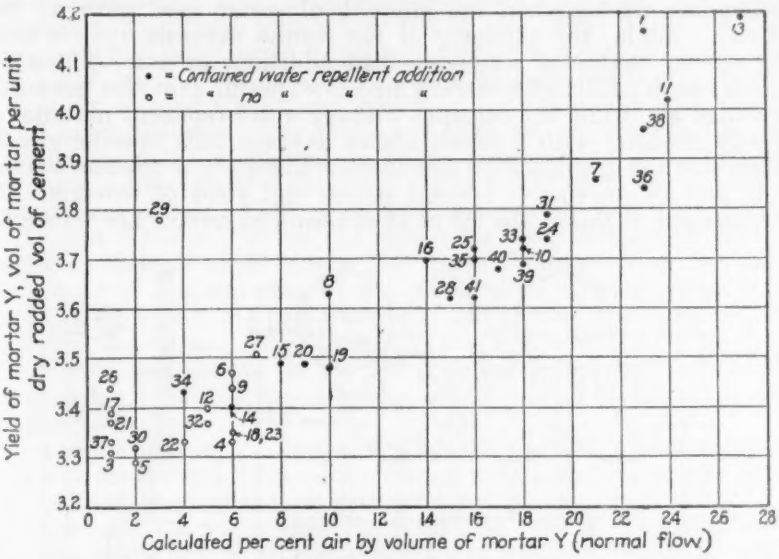
Yield of mortar Y, vol of mortar per unit dry rodded vol of cement
• = Contained water repellent addition
o = " no " " "
Calculated per cent air by volume of mortar Y (normal flow)

FIGURE 13.—*Relation of volume yield to amount of air present in mortar Y at normal flow.*

and hence, with two exceptions, those cements containing such additions gave mortars of high air content and high yield. Why two cements

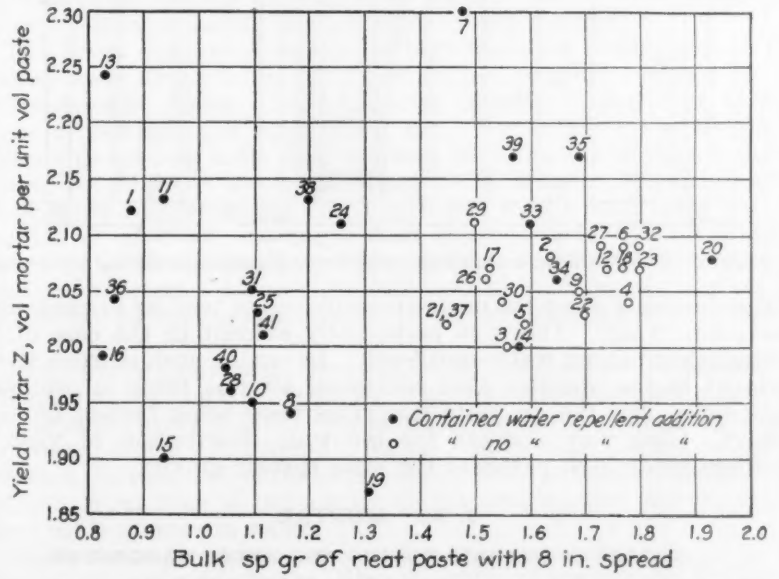
Yield mortar Z, vol mortar per unit vol paste
• Contained water repellent addition
o " no " " "
Bulk sp gr of neat paste with 8 in. spread

FIGURE 14.—*Relation between volume yield of mortar Z and the bulk specific gravity of the neat pastes.*

(nos. 14 and 34) are exceptions is not clear, although no. 34 contained such a small amount of the addition that it could not be identified.

Figure 14, in addition to giving data showing the yield of mortar Z, again presents the data showing the bulk specific gravities of the corresponding pastes when the amount of water used gave an 8-in. spread. Again, the grouping of the results depends upon whether the mortar contained water-repellent additions or not. Those containing such additions generally had low specific gravities because of occluded air, while the cements without water-repellent material are closely grouped with a much higher average bulk specific gravity. Otherwise the graph shows that there is but a slight relation between bulk specific gravity of cement pastes and yield of mortars. One explanation of this is the effect of the sand in mixing the mortars in

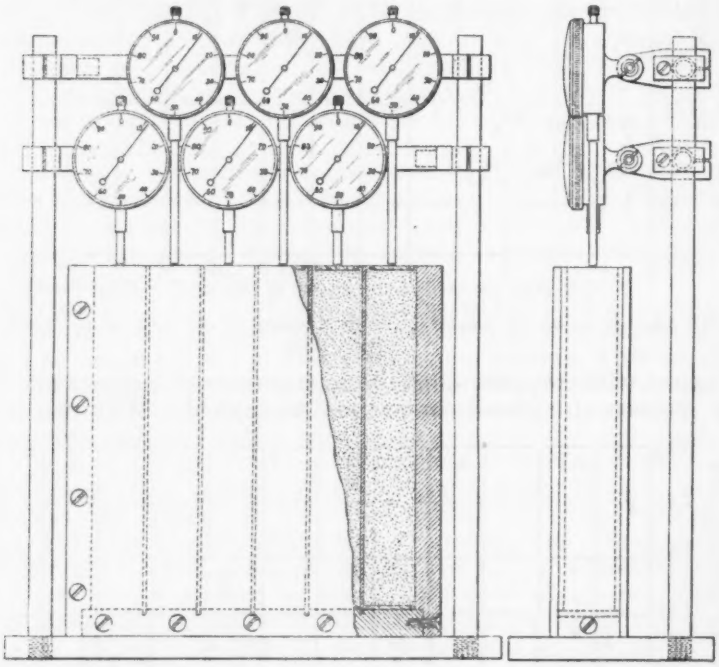

FIGURE 15.—*Device for measuring length change of specimens during hardening.*

either breaking down the paste-air emulsions or tending to cause more occlusion of air. This was particularly evident in the case of the cements containing water-repellents. In mixing such mortars it was evident to the operator that additional air was being incorporated into some, and the air-paste emulsions were being broken down in others. This may account for the wide distribution of yield of mortars made from pastes of the same specific gravity.

2. SET MORTAR

(d) LINEAR CHANGES DURING AND AFTER HARDENING

Specimens for one series of tests with mortar X were made with three different proportions of water, viz, that which produced a mortar having normal flow, that with 1 percent more, and that with 1 percent

less. The specimens were cast and measured during their hardening period in the apparatus shown in figure 15. The collapsible mold used was divided into six compartments, each 1 by 1 by 8 in. Each compartment was lined with waxed paper, and before filling with the mortar, a glass plate seven-eighths in. square was placed in the bottom. The mortar was gently rodded into each compartment and after filling, a small glass plate, similar to the one at the bottom, was placed upon the top. The mold was then set underneath the dial micrometers and the changes in length measured to 0.005 percent. The gages were so placed that their stems rested upon the centers of the top glass plates. They were read immediately and then hourly for the first 7 hours. When the specimens were sufficiently strong, usually at the end of 30 hours, they were removed from the mold and placed in a damp closet for 1 week, then in water storage for 1 week, after which one half were stored in air and the other half remained in the water. The changes in length during the damp closet storage were measured at the end of 3 days and 7 days, and later at the end of each week for the first 4 weeks, and thereafter at the end of each month.

Part of the data for the specimens gaged to normal flow are shown in table 3 in condensed form; these values were generally nearer those obtained with the higher than with the lower percentage of water.

The contraction noted while the specimens were in the molds was a resultant of the compacting of the mortars while in the plastic state, owing partly to the action of gravity, to the change accompanying the chemical reaction of the cement and water, and also possibly to the loss of air. The mortars made from cements having water-repellent additions shrank 0.043 percent more than those without, probably because of the greater amount of air incorporated. In a number of cases the changes during this period were very marked.

The linear changes in storage of high humidity subsequent to the setting were found to be of minor degree, possibly because of the heterogeneous nature of the cements—mostly mixtures of several types of cement, and lime, silica, etc. No data were available or obtainable on how individual cements in the mixtures deport themselves, but no doubt it would be possible to compound some mixtures so that the contraction of one constituent might counteract the expansion of another. Subsequent to setting, there was no marked difference in the linear change of the water-repelling and nonwater-repelling mortars. Hence, the addition of such agents cannot be considered as having contributed to the surprisingly small changes noted.

In the majority of cases, however, the shrinkage after hardening and during a year in the air was large. The data also show that a number of mortars having a large shrinkage in air have a relatively small increase in length when stored in water. Apparently the net change in length is the resultant of the shrinkage inherent in the hardening of the cement, regardless of the nature of the storage and the expansion expected in storage in water.

Table 3 also gives data showing linear changes of 1 by 4 by 12 in. bars which were subjected to alternate cycles of wetting and drying for 1 yr, and then broken transversely to obtain the moduli of rupture (fig. 18). Generally, these bars after 1 wk in the damp closet at 21° C were sufficiently strong to permit their being removed from the molds;

if not, they were allowed to remain until they could be more safely handled. After the first drying of 1 wk at 65° C they were placed in water for 1 wk at 21° C. This cycle was repeated until the end of the 38th wk. Then after drying for 1 wk, they were allowed to remain in water for 2 wk, dried for 1 wk, and then placed in water for 7 wk. The specimens were measured at the end of each period of storage. In the fifth and sixth columns of table 3 are given the shrinkages during the first and last periods of drying, respectively. In the seventh column the differences in length between the first and last dryings are shown.

TABLE 3.—*Percentage length changes of bars of mortar* X

[Blank spaces indicate the bars broke during handling before the measurements could be made]

1	2	3	4	5	6	7
	Bars 1 by 1 by 8 inches			Bars 1 by 4 by 12 inches		
Cement number	Shrinkage during first 24 hours	Length increase during 1 year in water	Shrinkage during 1 year in air	Shrinkage during first drying on removal from damp closet	Shrinkage during last drying at about 1 year	Change in length between first drying at about 1 week and last drying at about 1 year
1	0.256	0.040		0.154		
2	.307	.012	0.115			
3	.496	.038	.126	.068	0.038	+0.033
4	.087	.004		.040		
5	.499	.085	.070			
6	.196	.011	.120	.087	.046	+.010
7	.440	.057	.137	.102		
8	.585	.020	.164	.128	.034	+.016
9	.375	.013	.133	.091	.029	−.015
10	.384	.017	.098	.063	.036	−.032
11	.510	.090	.111	.026	.061	+.052
12	.484	.021	.109	.078	.077	−.012
13	.332	.121	.112	.124		
14	.218	.013	.065	.080	.032	+.021
15	.337	.011	.090	.071	.038	−.055
16	.340	.004	.122	.101	.032	−.065
17	.194	.051	.073	.075	.052	+.008
18	.216	.013	.055	.040	.027	−.006
19	.191	.016	.085	.074	.034	+.019
20	.131	.029	.069	.066	.039	+.057
21	.294	.027		.058	.010	+.022
22	.502	.053	.086	.059	.040	+.112
23	.166	.024		.043		
24	.406	.039	.090	.131		
25	.377	.030	.081	.067	.033	+.041
26	.268	.148	.052	.080		
27	.463	.016		.083	.019	+.031
28	.198	.019	.113	.092	.032	−.011
29	.216					
30				.069	.022	+.008
31	.345	.019	.195	.087	.042	−.023
32	.174	.009	.076	.069	.035	+.012
33	.220	.050		.036	.032	−.020
34	.255	.013	.103	.082	.032	+.019
35	.278	.009	.080	.072	.039	+.005
36	.309	.009	.096	.067	.028	−.027
37	.331	−.001	.116	.055	.023	+.007
38	.505	.025	.062	.068	.039	+.029
39	.330	.086	.070	.069		
40	.482	.014	.106	.089	.037	+.021
41	.494	.016	.101	.093	.037	+.008
Average	.335	.033	.099	.078	.036	+.012

A comparison of columns 4 and 5 shows that 1 wk's drying at 65° C, after about 1 wk's aging in the damp closet, produced almost as much shrinkage (in 6 cases somewhat more) as did 1 yr's drying at laboratory temperature. Indeed, if one is interested in quickly noting the relative degree of shrinkage during longer drying at normal temperature, it can be obtained by the procedure followed in securing the data of column 5. As the number of cycles of wetting and drying increased, the changes in length diminished with each cycle. Such cycles also generally resulted in the growth of the specimen. Plus signs in the seventh column indicate that the specimens were longer after the last drying than after the first, but not necessarily longer than the wet specimen before the first drying. The lengths of the specimens made from cements nos. 17, 22, and 26 were greater after the final than immediately before the first drying.

(b) COMPRESSIVE STRENGTH

The compressive strength of 2 in. cubes of mortars X, X–1, Y, and Z was studied. The amounts of water used in preparing these mortars, shown in table 2, were such that they were sufficiently workable to permit placing in the molds with a spatula. The filled molds were placed in a damp closet for 48 hr, after which the molds were removed. The specimens remained in the damp closet for 5 days longer, when the 7-day specimens were tested. The remaining specimens were then stored under water for a week. At that time one-half were removed and stored in air until tested, the other half remaining in the water. Three cubes after storage in the air and 3 after storage in water were tested at each of the following ages, 28 days, 3 mo and 1 yr.

Table 4 exhibits the compressive strengths. For the sake of brevity alone, the strengths of the mortars are presented as falling within certain groups. Such a presentation does not bring out clearly the effect of different amounts of water used in mortars X and X–1 or the gain in strength with age. But the masonry cements act like portland cements as far as increased amounts of water are concerned, and as the amount of water increases the strength decreases. Thus, while 8 of the cements in mortar X at 7 days gave strengths placing them in the highest class when the low percentage of water was used, but 3 were in this class when the high percentage was employed.

Cements with large proportions of portland cement gave mortars having greater strengths than those with small proportions, and such cements as hydraulic limes, while having little strength at early ages, increased in strength with time proportionately more than most of the others. It is evident that a wide variety of compositions may be used and good strengths obtained.

All cements in all the mortars showed good gain in strength with age, with the exception of a very few extremely high in hydrated lime. The rate of carbonation of such cements under the condition of storage was too low to be reflected in the strength at the ages at which tests were made. According to the table, the cements initially in group 7 appeared not to have gained strength with age. This is due solely to the fact that any mortar having a compressive strength over 2,000 lb/in.^{2} at any time would be shown as being in that group. Air storage usually gave higher strengths than water storage. The mixed sand of mortar X–1 produced mortars of greater strengths than the standard sand of mortar X.

TABLE 4.—*Results of compressive strength tests*

For brevity the strengths of the mortars are indicated as being within the following groups:

Groups	1	2	3	4	5	6	7
Failed (lb/in.²)	0 to 100	100 to 300	300 to 500	500 to 1,000	1,000 to 1,500	1,500 to 2,000	Over 2,000

[All specimens remained in molds for 48 hours, then in the damp closet for 5 days, after which they were stored either in water or in air]

Cement number	Mortar X												Mortar X-1			
	1 percent less water than normal flow				*N*=percent water for normal flow				1 percent more water than normal flow				1 percent less water than normal flow			
	Water storage				Air storage				Water storage				Air storage			
	7 da	28 da	3 mo	1 yr	28 da	3 mo	1 yr		7 da	28 da	3 mo	1 yr	28 da	3 mo	1 yr	
1	1	2	2	4	2	3	3		1	2	2	3	2	3	4	
2	3	3	4	4	4	5	5		3	3	4	4	4	5	3	
3	2	3	4	5	3	4	5		2	3	4	5	3	4	5	
4	3	4	4	6	4	5	5		3	4	4	5	4	5	5	
5	4	5	5	7	5	7	7		4	5	6	7	6	6	7	
6	4	7	6	7	5	7	6		5	7	7	7	7	7	7	
7	1	3	4	4	3	4	4		1	3	4	4	3	4	3	
8	7	7	7	7	7	7	7		7	7	7	7	7	7	7	
9	3	4	5	4	4	5	4		3	4	4	4	4	5	3	
10	4	5	6	7	6	6	7		4	5	6	6	5	5	6	
11	2	3	4	4	3	2	3		2	2	3	4	3	3	3	
12	3	4	6	7	5	5	5		2	4	6	7	5	5	6	
13	1	2	4	4	2	3	3		1	2	3	3	2	2	3	
14	5	5	7	7	6	7	7		4	5	6	7	6	7	7	
15	2	4	4	5	4	5	5		2	4	4	5	4	4	5	
16	4	5	6	7	6	6	6		4	4	5	6	4	5	6	
17	3	4	4	4	4	5	5		3	3	4	4	4	5	3	
18	5	7	7	7	7	7	7		5	6	7	7	7	7	7	
19	7	7	7	7	7	7	7		7	7	7	7	7	7	7	
20	7	7	7	7	7	7	7		7	7	7	7	7	7	7	
21	3	3	4	4	4	4	4		3	3	4	4	4	4	4	
22	4	5	5	6	6	6	7		4	4	5	5	5	6	7	
23	2	4	4	5	4	4	5		3	4	4	5	4	4	5	
24	6	7	7	7	7	7	7		5	7	7	7	5	7	7	
25	3	4	4	4	4	5	5		3	3	4	4	4	4	4	
26	2	3	3	3	4	4	4		2	2	3	3	3	4	4	
27	4	4	5	5	5	5	6		3	4	4	5	5	5	5	
28	7	7	7	7	7	7	7		7	7	7	7	6	7	7	
29	1	1	3	4	1	2	2		1	1	3	3	1	2	2	
30	3	4	4	4	4	4	5		2	3	4	4	4	4	5	
31	7	7	7	7	7	7	7		7	7	7	7	7	7	7	
32	7	7	7	7	7	7	7		6	7	7	7	7	7	7	
33	4	4	5	6	4	5	6		3	4	4	5	4	4	5	
34	5	5	6	6	6	7	7		5	5	6	6	6	7	7	
35	6	7	7	7	7	7	7		5	6	7	7	7	7	7	
36	5	6	5	7	6	6	7		4	5	6	5	6	7	6	
37	2	2	2	3	3	3	4		2	2	2	2	3	3	4	
38	6	7	7	7	7	7	7		6	7	7	7	7	7	7	
39	1	2	2	3	2	2	3		1	1	2	3	1	2	2	
40	7	7	7	7	7	7	7		7	7	7	7	7	7	7	
41	7	7	7	7	7	7	7		7	7	7	7	7	7	7	

Group	Number of different cements falling within each group															
1	6	1	0	0	1	0	0		5	2	0	0	1	0	0	
2	5	4	3	0	2	3	1		7	5	3	1	3	3	2	
3	8	6	2	3	4	3	4		8	7	4	5	6	3	6	
4	7	10	12	11	12	6	5		6	9	13	8	10	9	5	
5	4	6	6	4	3	9	9		6	5	2	8	4	8	7	
6	3	1	5	4	7	4	4		2	2	6	3	4	2	4	
7	8	13	13	19	12	16	18		7	11	13	16	13	16	17	

Group																
1	5	2	0	0	1	1	0		3	0	0	0	0	0	0	
2	9	6	3	2	4	4	4		7	4	2	1	2	1	2	
3	7	6	6	3	4	1	2		8	5	3	2	4	4	1	
4	8	10	12	8	11	12	9		4	11	10	12	11	5	6	
5	3	4	4	10	7	5	7		7	5	5	2	4	9	8	
6	6	4	6	4	2	4	4		2	4	7	7	6	3	4	
7	3	9	10	14	12	14	15		10	12	14	17	14	19	20	

TABLE 4.—*Results of compressive strength tests*—Continued

For brevity the strengths of the mortars are indicated as being within the following groups:

Groups	1	2	3	4	5	6	7
Failed (lb/in.²)	0 to 100	100 to 300	300 to 500	500 to 1,000	1,000 to 1,500	1,500 to 2,000	Over 2,000

[All specimens remained in molds for 48 hours, then in the damp closet for 5 days, after which they were stored either in water or in air]

Cement number	Mortar X-1—Continued								Mortar Y				Mortar Z			
	N=percent water for normal flow						1 percent more water than normal flow									
	Water storage				Air storage				Water storage		Air storage		Water storage		Air storage	
	7 da	28 da	3 mo	1 yr	28 da	3 mo	1 yr	7 da	28 da	3 mo	1 yr	28 da	3 mo	1 yr	7 da	28 da	3 mo	1 yr	28 da	3 mo	1 yr
1	1	2	3	4	2	4	4	1	2	3	3	3	3	2	1	1	2	2	2	2	2	1	1	2	2	2	2	2
2	3	4	3	5	5	5	4	3	4	4	4	4	5	5														
3	2	3	3	5	4	4	4	2	3	4	5	4	4	5	1	1	2	3	2	2	2	2	3	4	4	4	4	4
4	3	4	5	6	4	5	5	3	5	4	6	4	5	5	2	3	3	4	3	3	3	4	5	5	5	5	4	5	5
5	4	5	5	7	6	7	7	4	5	6	6	5	6	7	2	3	3	4	3	4	4	4	5	6	6	6	7	6
6	5	6	7	7	7	7	7	5	5	7	7	6	7	7	3	4	5	5	5	5	5	5	7	7	7	7	7	7
7	2	3	3	5	3	4	4	2	3	4	5	3	4	3	1	2	4	4	2	3	3	3	4	5	3	4	4	4
8	7	7	7	4	7	7	7	7	7	7	7	7	7	7	5	6	7	7	7	7	7	6	7	7	7	7	7	7
9	3	4	3	4	5	5	4	3	4	4	4	5	5	3	2	2	2	3	2	2	2	3	4	4	3	4	4	4
0	4	5	6	7	5	7	7	4	5	6	6	6	6	6	3	4	4	5	4	4	4	4	5	6	6	5	6	6	5
11	2	3	4	4	3	3	4	2	2	4	4	3	3	3	2	2	2	3	2	2	2	2	2	3	3	2	3	2
12	3	4	6	6	5	6	5	3	4	6	7	5	6	5	2	3	4	4	3	4	4	3	5	7	7	6	7	7
13	1	3	4	4	3	3	4	1	3	3	3	3	2	3	1	2	2	3	2	2	2	1	2	2	2	2	2	2
14	4	5	7	7	7	7	7	4	5	6	7	6	7	7	2	3	3	4	4	4	4	5	6	7	7	7	7	7
15	3	4	3	6	4	5	5	2	4	4	5	4	5	6	2	3	4	4	3	4	3	2	3	3	4	3	4	3
16	4	5	5	6	5	5	5	4	4	5	6	5	5	6	2	2	3	4	3	3	3	2	3	4	4	3	3	4
17	3	3	4	5	4	5	4	2	3	4	4	4	4	4	1	2	2	2	2	2	2	3	4	4	4	4	5	5
18	5	7	7	7	7	7	7	5	7	7	7	7	7	7	3	4	5	6	7	7	6	6	7	7	7	7	7	7
19	7	7	7	7	7	7	7	7	7	7	7	7	7	7	6	7	7	7	7	7	7	7	7	7	7	7	7	7
20	7	7	7	7	7	7	7	7	7	7	7	7	7	7	6	7	7	7	7	7	7	7	7	7	7	7	7	7
21	2	3	4	4	4	4	4	2	3	4	4	4	4	4	2	2	2	2	2	2	2	2	3	4	4	4	4	4
22	5	4	6	6	3	7	7	4	4	5	6	4	6	6	2	3	3	3	3	4	4	5	6	6	7	7	7	7
23	3	4	4	5	4	4	4	3	4	4	5	4	4	5	2	3	4	4	2	3	2	4	5	5	6	5	5	6
24	6	7	7	7	7	7	7	5	5	7	7	7	7	7	4	5	6	6	5	6	5	4	6	7	7	6	7	7
25	3	3	4	4	4	5	5	3	3	4	4	4	4	4	2	2	2	3	3	3	3	2	2	3	3	4	3	4
26	2	3	3	4	3	4	4	2	2	3	3	4	4	4	1	1	2	2	2	2	2	2	2	3	3	3	4	4
27	4	4	5	5	5	5	5	4	4	5	5	5	6	5	2	3	3	4	4	4	4	4	5	6	6	6	7	6
28	7	7	7	7	7	7	7	7	7	7	7	7	7	7	6	7	7	7	7	7	7	5	7	7	7	7	7	7
29	1	1	3	4	1	2	2	1	1	3	4	1	1	2	1	1	2	3	1	1	1	1	2	3	4	1	2	2
30	2	3	4	4	4	4	5	2	4	4	4	4	4	4	1	2	2	2	2	2	3	5	6	7	4	7	6	5
31	7	7	7	7	7	7	7	6	7	7	7	7	7	7	6	7	7	7	7	7	7	5	6	7	7	7	6	7
32	6	7	7	7	7	7	7	6	7	7	7	7	7	7	4	4	5	5	5	5	5	7	7	7	7	7	7	7
33	3	4	5	5	4	5	5	3	4	4	5	4	4	4	2	3	4	5	3	4	4	3	4	4	5	4	5	5
34	5	5	6	6	6	7	7	5	5	5	6	6	6	7	3	3	3	4	4	4	4	6	6	7	7	7	7	7
35	6	7	7	7	7	7	7	5	5	7	7	7	7	7	4	5	5	5	5	5	5	6	7	7	7	7	7	7
36	4	6	6	6	6	7	6	4	5	5	5	6	6	5	4	4	4	4	5	5	5	3	4	4	4	4	4	4
37	2	2	2	2	3	3	3	2	2	2	2	2	3	2	1	1	1	1	1	1	1	2	2	2	2	3	3	3
38	7	7	7	7	7	7	7	6	7	7	7	7	7	7	5	6	6	6	6	6	7	5	6	6	7	6	6	7
39	1	2	2	3	2	2	2	1	1	2	3	2	2	2	1	1	1	2	1	2	2	1	2	2	3	2	2	3
40	7	7	7	7	7	7	7	7	7	7	7	7	7	7	6	7	7	7	7	7	7	6	7	7	7	7	7	7
41	7	7	7	7	7	7	7	7	7	7	7	7	7	7	6	7	7	7	7	7	7	6	7	7	7	7	7	7

Group	Number of different cements falling within each group																							
1	4	1	0	0	1	0	0	4	2	0	0	1	1	0	10	6	2	1	3	2	2	4	1	0	0	1	0	0
2	7	3	2	1	2	2	2	9	4	2	1	2	2	4	14	9	11	6	11	10	10	9	7	4	3	5	4	4
3	9	9	8	1	6	3	1	7	6	4	4	4	3	4	4	10	7	7	7	5	6	5	5	5	4	4	4	3
4	6	9	7	10	9	7	11	7	10	13	8	12	9	6	4	5	7	11	5	9	8	6	4	8	8	8	7	8
5	4	5	5	7	6	9	8	5	9	5	7	5	5	6	2	2	4	5	5	4	5	7	6	2	4	2	4	5
6	5	2	5	7	3	1	1	3	0	4	6	5	7	5	6	2	2	3	1	2	1	6	7	5	4	5	4	3
7	6	12	14	15	14	19	18	6	10	13	15	12	14	16	0	6	7	7	8	8	8	3	10	16	17	15	17	17

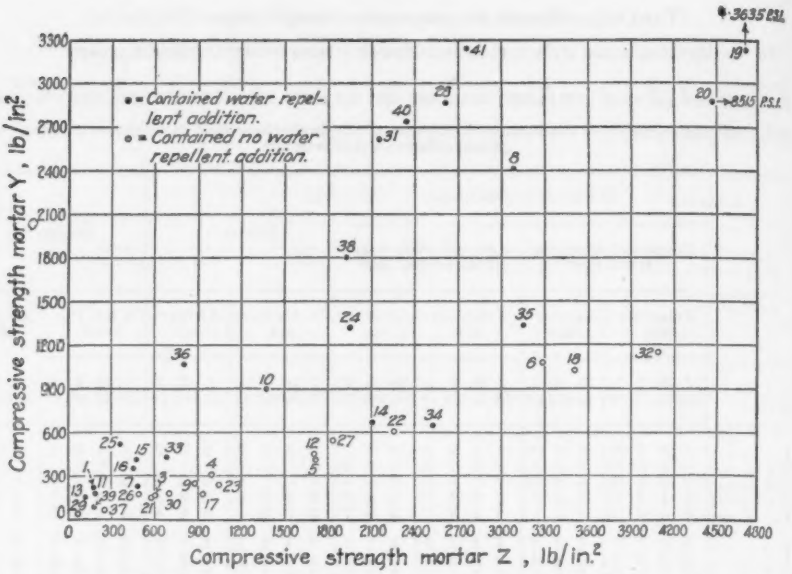
Compressive strength mortar Y, lb/in.²
Compressive strength mortar Z, lb/in.²
• = Contained water repellent addition.
• = Contained no water repellent addition.
3635 P.S.I.
8545 P.S.I.

FIGURE 16.—*Relation between 28-day compressive strength of mortars* Y *and* Z *at normal flow.*

Two-inch cubes stored in damp closet 7 days at 21° C, then 7 days submerged in water, then 14 days in air at 21° C, 60±5 percent relative humidity.

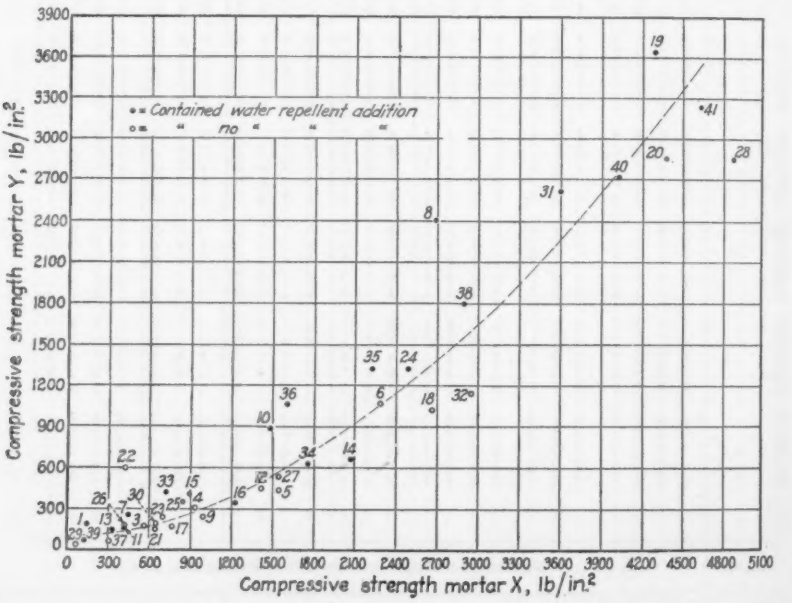

FIGURE 17.—*Relation between 28-day compressive strength of mortars* X *and* Y *at normal flow.*

Two-inch cubes stored in damp closet 7 days at 21° C, then 7 days submerged in water, then 14 days in air at 21° C, 60±5 percent relative humidity.

While in a general way it might be said that the mortars of the Y type had less strength than those of the X or the X–1 types, and that mortar Z was between these types, some interesting relations can be noted on comparing figures 16 and 17. In the former figure the strengths of the air-stored specimens at 28 days of mortars Y and Z are presented. The classification of the mortars of the water-repellent and nonwater-repellent cements is again evident with the usual few exceptions. Mortars of the Z type tend to have strengths somewhat greater than those of the Y type; again those of the Z type not containing the water-repellent additions are 3 to 4 times as strong as those of the Y type at 28 days. All mortars X without water-repellent cements except no. 22 are within the range of 2 to 4 times the strength

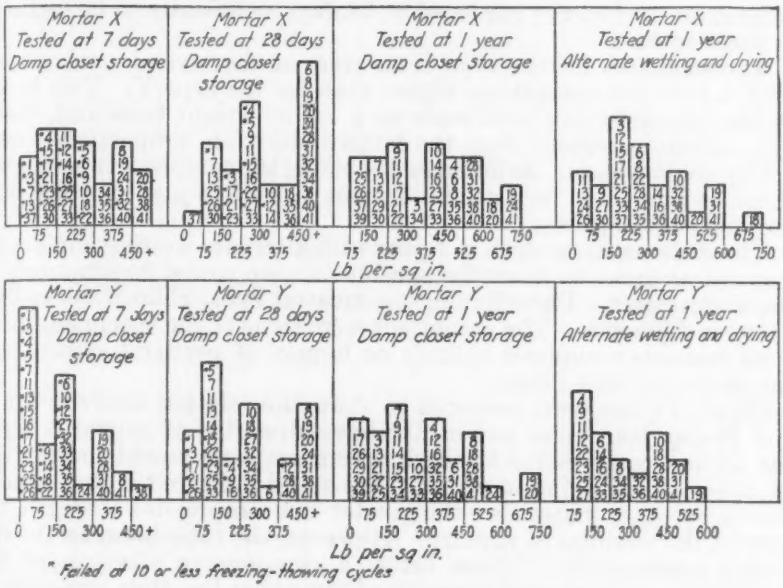

FIGURE 18.—*Moduli of rupture mortars* X *and* Y.

Cement no. 2 not tested in any storages shown; cement no. 5 not tested in the cases of 1-year damp closet, nor alternate wetting and drying because the supply of the cements was exhausted. Specimens made from other cements not represented in these histograms broke during storage.

of mortars Y, while only 7 of those with water-repellent cements are within that range. All but 7 of the first class are within the range 3 or 4 times as strong. The explanation can possibly be found by consulting tables 1 and 2 and noting the volume weights of the cements and the weight proportions of the mortar. The Z mortars made from nonwater-repellent cements were usually richer in cement than those made of the water-repellent ones. This resulted from the differences in the bulk specific gravities of the neat pastes.

Figure 17 shows the relation between the compressive strength at 28 days' air storage of the cements when used in mortars X and Y. Here it will be noted that the relation is markedly different from that exhibited in comparing mortars Y and Z (fig. 16). Mortar X was proportioned on a 1:3 by weight basis and mortar Y on a 1:3 by volume. Hence it will be noted that when the cements had low weight per cu ft the cements in mortar X developed approximately 3 times

the strength which they produced in mortar Y, but as this weight increased the 1:3 volume mortars approached the same weight ratio as used in mortar X and the strengths more nearly approached one another. The portland cements or those having a large proportion of portland cement gave mortars of nearly equal strengths.

(c) TRANSVERSE STRENGTH

Specimens of mortars X and Y, 1 by 4 by 12 in., were tested flatwise for transverse strength with a center load on a 10-in. span, the load being applied on the top of the specimen as cast. These were proportioned as shown in table 2 for normal flow. The curing conditions and results of tests are given in figure 18. The molds were removed at 24 hr or as soon thereafter as possible. Specimens of cement no. 29 had not hardened at 28 days sufficiently to be included in these tests.

The strengths for the type X mortars of the several cements are, with a very few exceptions, higher than for the type Y. This is due to the former having been made on a 1:3 by weight basis and, therefore, richer in cement than the latter, which are proportioned on a 1:3 by volume basis. As noted in discussing the compressive strengths, those cements rich in portland cement tended to give mortars with the higher strengths.

The increase in strength in 1 year with alternate wetting and drying was not as great as when the specimens were stored continuously in the damp closet. Those having the greatest linear change showed the greatest difference. The exceptions were some of the specimens made from cements composed entirely or largely of portland cement and the one of hydrated lime.

Figure 19 has been prepared to show the relation between the 7- and 28-day transverse and compressive strengths of mortar Y when the 28-day compressive strength specimens were stored for the last 21 days of their aging in water. The trend indicated is that usually shown by other materials—the greater the compressive strength, the greater the modulus of rupture. However, the ratio between the two varies considerably. Those below a compressive strength of 900 lb/in.^{2} have a transverse strength of somewhat less than one-third of the compressive strength, while above 900 lb/in.^{2} the values change until at the higher strength the ratio is approximately 1:6. The compressive strengths for the majority of the specimens of mortar Y tested both at 7 and 28 days were below 900 lb/in.^{2} and the modulus of rupture below 300 lb/in.^{2}

(d) DURABILITY IN FREEZING AND THAWING TESTS

One of the halves of each specimen remaining after the transverse tests were made, at both 7 and 28 days, was submitted to freezing and thawing cycles. One cycle consisted in freezing for 24 hr, flatwise in about ½ in. of water, followed by 24 hr of thawing in water at room temperature. The results are presented in table 5.

It is seen that there is little difference in the destructive action of freezing and thawing on the rich mortar X and on the leaner mortar Y. Comparing these results with the compressive and transverse strengths it was noted that those mortars which had a low strength, or low modulus, with the exception of the specimen made of cement no. 11, showed poor resistance. As previously noted, the higher strengths generally resulted when the mortars contained cements rich in portland cement.

Aging the specimens until 28 days before starting the freezing and thawing, instead of but 7 days, permitted a few of the mortars to

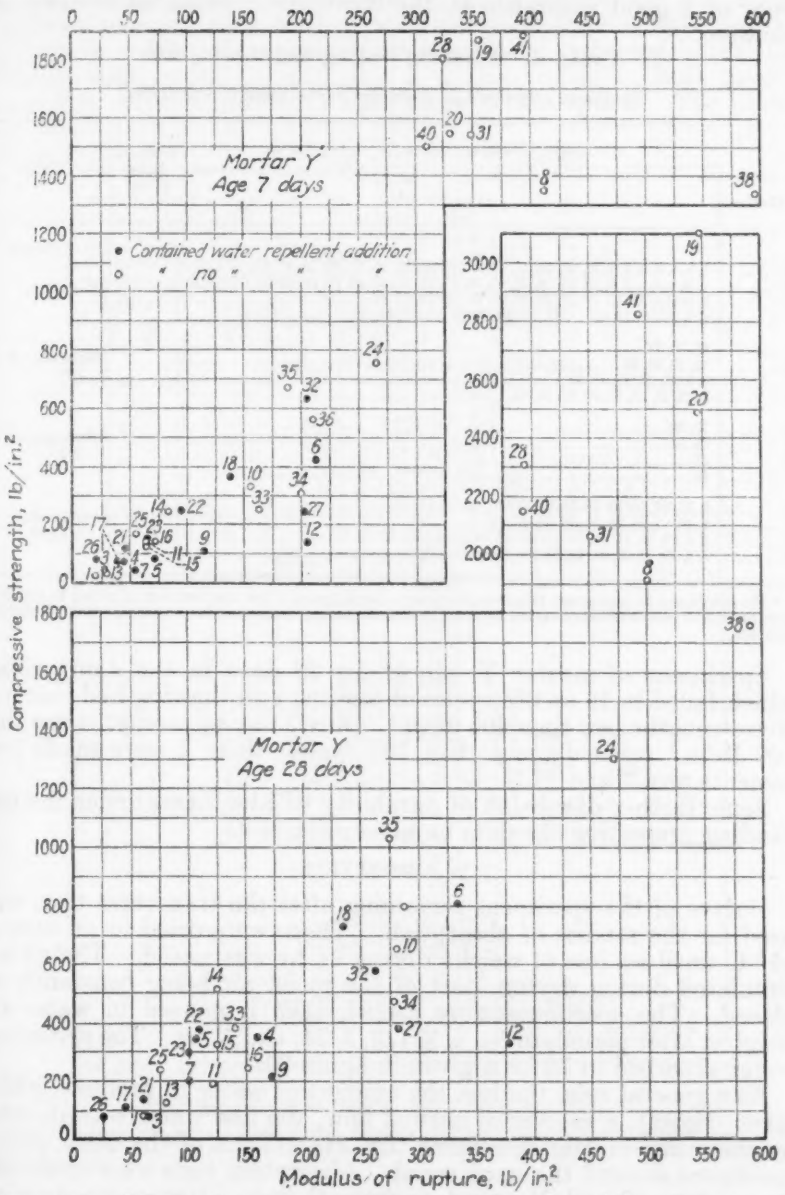

FIGURE 19.—*Relation between compressive strength and modulus of rupture for mortar* Y.

All 2-inch cubes for compressive strength were stored in the damp closet at 21° C for 7 days. The 28-day specimens were stored in water at 21° C for 21 days. The specimens for transverse tests were stored continuously until breaking date in the damp closet at 21° C.

develop better resistance. Such usually showed good compressive strength gains between 7 and 28 days. A surprising feature of these

tests is that relatively few specimens were in the group that failed between 10 and 300 cycles. Most of the mortars had either a very poor or a good resistance to the destructive action of freezing and thawing.

TABLE 5.—*Results of freezing and thawing tests*

[Specimens 1 by 4 by 6 in. made from mortar gaged to normal flow]

Materials		Days in damp closet	Failed
Mortar	Cement		
			(*Cycles*)
X	1, 3, 4, 5, 6, 7, 9, 12, 13, 14, 15, 17, 21, 22, 23, 25, 26, 27, 29, 32, 37, 39	7	10 or less.
Y	1, 3, 4, 5, 6, 7, 9, 12, 13, 14, 15, 17, 18, 21, 22, 23, 25, 26, 27, 29, 30, 32, 37, 39		
X	1, 3, 4, 5, 12, 15, 17, 21, 22, 23, 26, 27, 29, 30, 37, 39	28	
Y	1, 3, 4, 5, 9, 12, 15, 17, 21, 22, 23, 26, 29, 30, 37, 39		
X	18, 30, 33	7	Between 10 and 100.
Y	16, 20, 33, 35		
X	6, 9, 13, 18, 25, 32, 33	28	
Y	6, 13, 14, 16, 18, 25, 27, 32, 33		
X	19, 20	7	Between 100 and 250.
Y	19, 34		
X	14	28	
Y	19		
X	8, 10, 11, 16, 24, 28, 31, 34, 35, 36, 38, 40, 41	7	Over 250.* No failures.
Y	8, 10, 11, 24, 28, 31, 36, 38, 40, 41		
X	7, 8, 10, 11, 16, 19, 20, 24, 28, 31, 34, 35, 36, 38, 40, 41	28	
Y	7, 8, 10, 11, 20, 24, 28, 31, 34, 35, 36, 38, 40, 41		

* No specimens in this group failed—testing was discontinued when the number of cycles to which the specimens had been subjected varied from 335 to 460, the earlier-made specimens having received the larger number.

Specimens of mortar Y, stored for 28 days in the damp closet, which failed in 10 or less cycles of freezing and thawing had compressive strengths less than 400 lb/in.^{2} Only 2 having strengths less than 400 lb/in.^{2} resisted more than 100 cycles; these 2 were made from cements nos. 7 and 11.

Some further discussion of durability will be found under the next heading presenting the data on absorption tests.

(e) ABSORPTION

Halves of the specimens remaining after the transverse tests were used for the studies of absorption. These were dried in an oven at 65° C until no loss of weight during 24 hr was noted. The air was circulated during drying, part of the moist air being constantly replaced. The specimens were cooled, then immersed in water and weighed after periods of $\frac{1}{12}$, $\frac{1}{4}$, $\frac{1}{2}$, 1, 3, 5, 24, and 72 hr. The percentage water absorbed in 72 hr is given in figure 20.

As a general rule, the less the amount of water to produce, with a given cement, a mortar of normal flow, the less water was absorbed by the cured mortar specimens (fig. 21). Tests of the other mortar specimens showed the same trend. Absorption tests were made only on mortars X and Y gaged to normal flow. Hence, no data are available showing how any of the cements varied in absorption when gaged with different amounts of water.

It is of interest to compare figures 22 and 13. The former presents the relation of the bulk specific gravity of mortar Y to the percentage water absorbed by the specimens of that mortar after 7 days' aging, also the results of freezing and thawing tests. (Similar relations were

found for this mortar at other intervals during absorption tests and after 28 days of aging.) Again the cements group themselves according to presence or absence of water-repellent materials. The water-repellent mortars may have a wide range in bulk specific gravity without a corresponding range in absorption, whereas in mortars lacking water-repellent materials a narrow range in bulk specific gravity is accompanied by a wide range in absorption. The porous

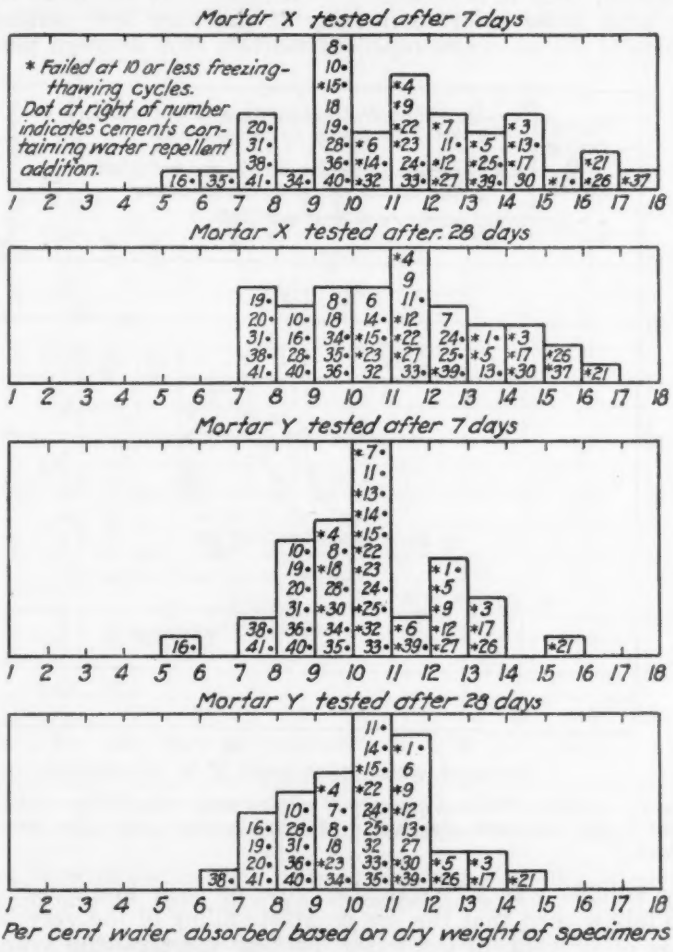
Mortar X tested after 7 days
* Failed at 10 or less freezing-thawing cycles.
Dot at right of number indicates cements containing water repellent addition.
Mortar X tested after 28 days
Mortar Y tested after 7 days
Mortar Y tested after 28 days
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Per cent water absorbed based on dry weight of specimens

FIGURE 20.—*Absorption, 72 hours total immersion.*

Specimens made from cement no. 29, mortar X, crumbled when immersed; specimens made from cements nos. 29 and 37, mortar Y, crumbled when immersed. Cement no. 2 not shown because supply of cement was exhausted.

structure of those specimens made from mortars of a high air content, as shown in figure 13, would, in the specimens having high absorption, be expected to be disrupted with freezing. Such was not always the case. Hence, it would appear that the failures are not due solely to the expansion in the water-filled air cells during freezing, but more to the freezing of the water-saturated partially hydrated cement of the cell walls.

Kreuger[6] in a study of the weathering resistance of burned clay materials proposed the ratio of absorption at 4 days to porosity obtained by specific gravity determinations as an indication of resistance. Data for the calculation of the Kreuger ratio for the mortar specimens were not complete, but there was evidence that the water-repellent mortars had lower ratios than most of the others and their resistance was good. If the explanation in the preceding paragraph is accepted, then it is necessary to assume that the more complete filling with water prior to freezing of the very low percentage of air voids of the nonwater-repellent mortars (the average percentage

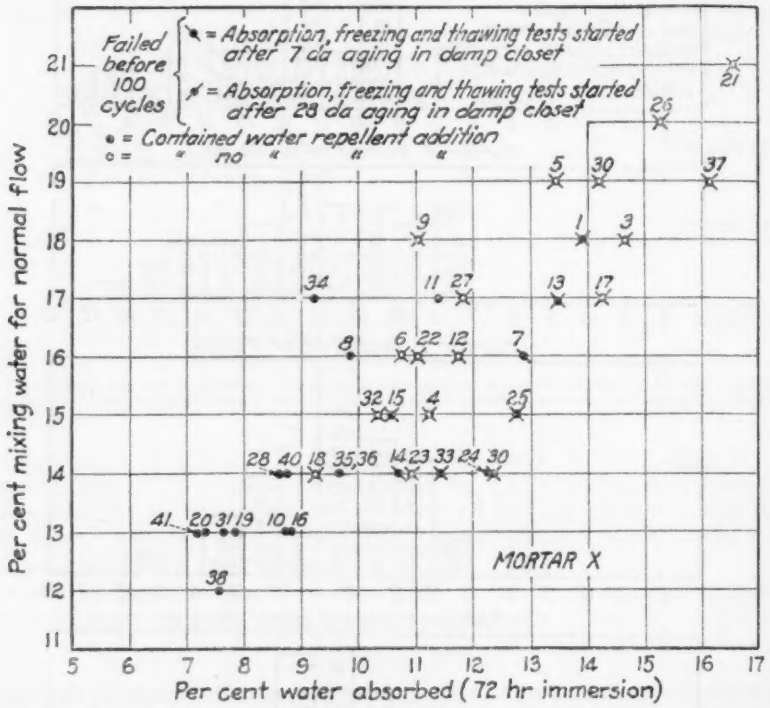
Failed before 100 cycles
= Absorption, freezing and thawing tests started after 7 da aging in damp closet
= Absorption, freezing and thawing tests started after 28 da aging in damp closet
• = Contained water repellent addition
○ = " no " " "
Per cent mixing water for normal flow
Per cent water absorbed (72 hr immersion)
MORTAR X

FIGURE 21.—*Relation between quantity of mixing water required for normal flow for mortar X and the water absorbed in 72 hours by this mortar after being aged for 28 days.*

air by volume was 3.7) was the cause of their low resistance. It would follow then that the less complete filling of the very high percentage of air voids of the water-repellent mortars (the average percentage air by volume was 19.53) was the reason for their good resistance. The voids resulting from the loss of mixing water due to hydration, evaporation, etc., are not considered here. The voids from this source were about equal for the water-repellent and nonwater-repellent mortars, although there was a slight tendency for the water-repellent mortars to require less mixing water than the others.

A study of the rate of absorption brought out the fact that the first 90 percent of the absorption at 72 hr took place relatively rapidly. All but 10 percent of the absorption in mortars X and Y had, in about

[6] Trans. Roy. Swed. Inst. Sci. Ind. Res. **24**, 70 (1923).

half of the specimens, taken place in less than 1 hr. Further, as shown by figure 23, there seemed to be a relation between the time for mortars to attain 90 percent of the 72 hr absorption and the resistance to the destructive action of freezing and thawing. The poorly resisting mortars of the X and Y types have an absorption equal to 90 percent of that measured in 72 hr within ½ hr) when the determinations were made on specimens aged for 7 days, and within 1 hr when the determinations are made on the 28-day specimens. The mortars of the Y type being somewhat lean usually had a faster rate of absorp-

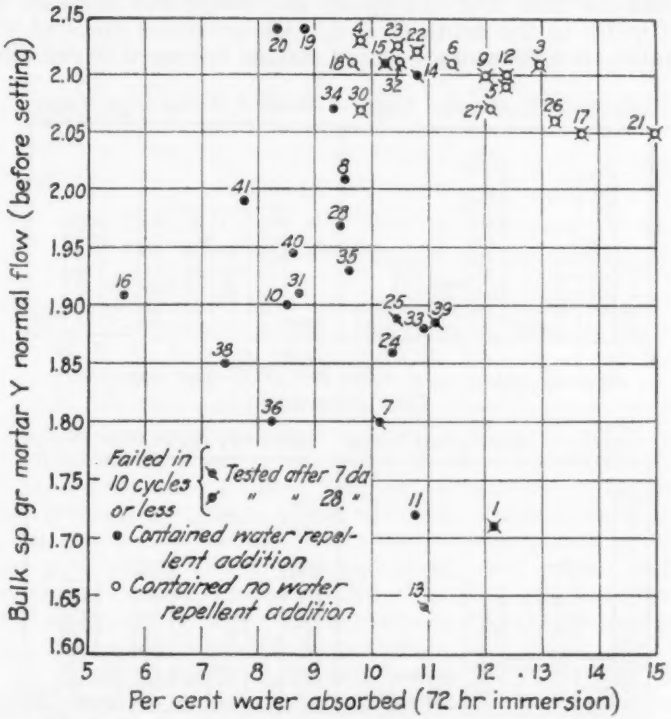

FIGURE 22.—*Relation between bulk specific gravity mortar Y and 72-hour absorption of the same mortar after being aged for 7 days.*

Specimens made from cements nos. 29 and 37 disintegrated during the test.

tion than those of the richer X type. Mortars Y made from cements nos. 11, 24, and 27, aged 28 days, are exceptions.

(*l*) WATER RISE DURING PARTIAL IMMERSION

After the previous weight-absorption study had been completed, the specimens were again dried to constant weight at 65° C. They were then cooled to room temperature and placed on end in ½ in. of water and the water line or height to which the specimens became wetted was measured at 1/12, ¼, ½, 1, 3, 5, 24, and 72 hr. Measurements were made to the nearest 0.1 in. on both the sides which had been the top and bottom of the specimen when molded. The average of the 2 measurements was recorded.

The data are not presented here, but it was found that the linear rise in the partially immersed specimens also would serve as an indi-

cation of durability. Of those mortars with a 2-in. rise in 1 hr or less, all failed in 10 or less cycles of freezing and thawing. In 59 out of 71 cases those mortars which showed a 2-in. rise in 3 hr or less failed in 10 or less cycles of freezing and thawing. The leaner mortar Y showed a more rapid rise than mortar X, and with both types the rise at 7 days' age was more rapid than at 28 days.

(g) EFFLORESCENCE

The tendency of the cements to effloresce was studied by placing the specimens that had undergone the absorption tests on end in trays of water to the depth of ½ in. Observations made at the end of 3 months after the storage period started appeared to represent the

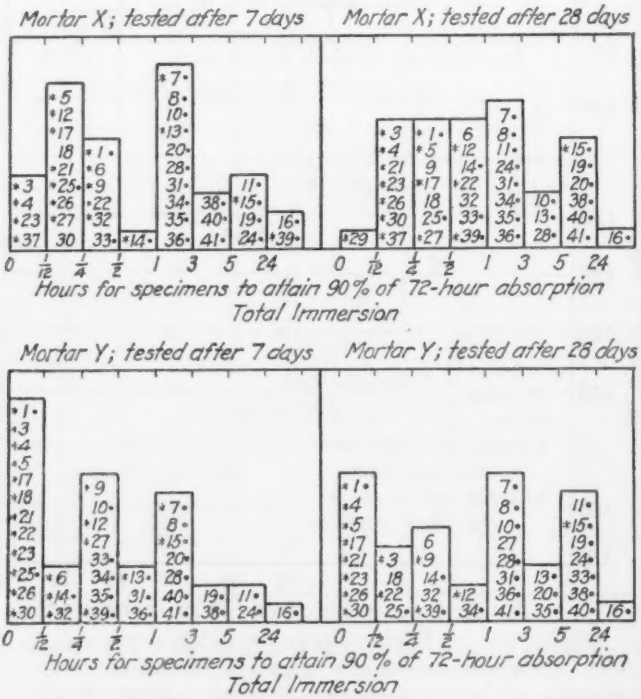
Mortar X; tested after 7 days
Mortar X; tested after 28 days
Hours for specimens to attain 90% of 72-hour absorption
Total Immersion
Mortar Y; tested after 7 days
Mortar Y; tested after 28 days
Hours for specimens to attain 90% of 72-hour absorption
Total Immersion

FIGURE 23.—*Time required for mortars to attain 90 percent of the 72-hour absorption.*

* Failure of specimens in 10 or less freezing-thawing cycles. Dot at right of numbers indicates cements containing water-repellent addition.
Specimens were 1 by 4 by 6 in.

maximum condition of efflorescence. Slight efflorescence was noted with:

Cements nos.[7] 11 (b), 12 (e), 13 (b), 24 (b), and 39 (d) of mortar X subjected to test after 7 days' aging;

Cements nos. 8 (a), 12 (e), 13 (b), 24 (b), and 31 (a) of mortar X subjected to test after 28 days' aging;

Cements nos. 9 (e), 11 (b), 13 (b), 16 (b), 23 (e), 34 (d), and 39 (d) of mortar Y subjected to test after 7 days' aging;

Cements nos. 5 (e), 7 (b), 13 (b), 16 (b), 23 (e), 24 (b), 30 (e), 31 (a), and 39 (d) of mortar Y subjected to test after 28 days' aging.

[7] Letters in parentheses refer to water-repellent additions. See table 1 for legend.

NOTE

The two closing sentences of section "(g) Efflorescence," page 845, Research Paper 746, should read:

the number and description of the cements that effloresced slightly or pronouncedly are as follows:-

one of the seven classed as "largely portland cement,"
two of the two classed as "portland cement and natural cement,"
three of the eight classed as "portland cement and lime,"
two of the ten classed as "portland cement and unidentified material,"
none of the two classed as "hydraulic or hydrated lime,"
four of the four classed as "natural cement,"
two of the six classed as "large amounts of slag,"
one of the two classed as "composition unidentified."

Pronounced efflorescence was noted with:

Cements nos. 1 (a) and 7 (b) of mortar X subjected to test after 7 days' aging.

Cements nos. 1 (a), 7 (b), and 11 (b) of mortar X subjected to test after 28 days' aging;

Cements nos. 1 (a), 5 (e), and 7 (b) of mortar Y subjected to test after 7 days' aging;

Cements nos. 1 (a) and 11 (b) of mortar Y subjected to test after 28 days' aging.

The other cements did not develop efflorescence in either mortar.

Efflorescence developed through such a test depends upon the composition of the cement. But again, owing to the heterogeneous nature of the cement, it is difficult to draw any positive conclusions as to the rate of solution of any of the components of the cement and their deposition on dry parts of the mortar. It will be noted that cements 5, 9, 12, 23, and 30 did not have water-repellent materials, while cements nos. 1, 7, 11, 13, 16, 24, 31, 34, and 39 had such additions. All except no. 5 of those showing pronounced efflorescence had water-repellent additions. All cements containing natural cement, 1 portland cement, 1 of portland cement and lime, 2 of the 4 slag cements, 2 of the unidentified composition effloresced. No efflorescence was observed with cements nos. 3 and 37.

V. DISCUSSION

The number of tests required by specifications for masonry cements should be held to a minimum and confined to those that can be completed in a relatively short time. It is, therefore, desirable to study the essential properties to find possible correlations between them and to see if the measurement of one will give an indication of another. Among the properties that are of interest are workability, durability, strength, absorption, linear changes during and after hardening, water-retaining capacity, volume yield of mortar, and range in water content of workable mortar. These properties have been enumerated without regard to their relative importance.

Two of these properties—durability and linear change—can be determined only by tests that require a longer time than would be convenient for an acceptance test. There seems to be no relation between the linear changes and the other properties of the mortars. While but a small change is desirable, the data are not conclusive enough to indicate the maximum amount permissible, although they indicated that the changes were so large as to be a matter of some concern. Although the changes during setting seem large, these changes might be neglected if they take place before rigidity is acquired by the mortar. The cracks frequently noted in vertical joints of masonry between the mortar and the brick or stone might be due in part to the large change in volume of the mortar during setting, or to stresses set up during that period which with subsequent slight contraction would yield cracks. But further work should be done in the study of this problem, and it is a question if it should not be an item in all cement specifications.

Durability as measured by the freezing and thawing tests may be predicted with fair accuracy from the rate of absorption of specimens 1 by 4 by 6 in. aged 28 days, and with less assurance with those aged

7 days. The absorption at 28 days is, therefore, suggested as a specification requirement for the indication of the durability. A requirement that the 1 hr absorption of a 28-day-old mortar shall not exceed 90 percent of the 72 hr absorption will, in the majority of cases, eliminate those cements which would make a mortar that will not endure 10 or more cycles of freezing and thawing.

The modulus of rupture and the compressive strength have sufficient relation to one another to permit the use of only one of these criteria as a measure of the strength. By reason of the relative ease of fabricating and testing, the 2-in. cube made of graded sand, of 1:3 proportion by weight at approximately normal flow, is suggested as a test specimen.

The strength that should be required is a matter of conjecture. A moderate or even a low strength would be sufficient in many cases. But in masonry construction where hollow thin walled units are used, a high-strength mortar is essential. It might be desirable to have 2 classes of strength—a higher and a lower one—and permit the specification writer to indicate that which he feels is required. In such a case, the lower strength requirement might have a minimum of 250 lb/in.^{2} at 7 days, and 400 at 28 days, and the higher demand a strength of 1,000 lb/in.^{2} at 7 days, and 1,500 at 28 days.

Mortars should retain their workability for a short time while in contact with a dry brick of moderately fast rate of absorption. The workability characteristics should be determined by studying the properties, stirring resistance, and water-retaining capacity together. For example, mortars made from cements that have a wide water-range could be prepared with the greater proportions of mixing water so that the mortars would retain their workability when exposed to absorptive units, or cements that have a narrow water range and yet have a sufficiently high water-retaining capacity to remain in the workable range. It was observed that the cements that required small amounts of water for the desired degree of workability and retained their workability in the presence of an absorptive unit usually had other good characteristics. In view of the unusual equipment needed to measure these two properties, it is suggested that this should be a subject for further consideration. The cements tested that retained not less than 0.9 and 0.85 of the mixing water at normal flow for 1 and 3 min. of suction, respectively, retained a satisfactory workability.

The volume yield of the mortar is primarily of economic importance. But it is so much influenced by the amount of occluded air that even though the air has a markedly favorable influence on workability and no deleterious effect on durability, it might seem to be desirable to have a maximum limit on the yield.

Observations in actual service of products bonded by hydraulic cements show that the denser products have greater life. There is no correlation at present between service results and laboratory data, therefore no limits are proposed for the amount of occluded air.

The majority of these masonry cements have been on the market for this purpose but a relatively short time. Their development seems to have been largely empirical, and it is believed that some of the methods of study used in this investigation would be of value to manufacturers in improving their products. Thus, the measurement of the water range within the limits of high and low stirring resistance would be of value when considered in conjunction with the water-

retaining capacity. If these properties are not satisfactory, he can be assured that his product is not on a parity with cements of wider adaptability.

The manufacturer should consider the several phases of workability. Does his cement give workable mortars with high percentages of water or with low? Is such workability accompanied by a large or small inclusion of air? Has the acquiring of workability been accompanied by lower strengths? What are the nature and economy in the use of the agent added to secure workability? These and other items are of much importance in the development of cements for setting masonry, and through their study it seems very likely that such cements will approach much more closely standard products of rather similar nature and properties than at the present time.

The composition of masonry cement seems to be the feature most affecting durability to freezing and thawing, although the effect of the varying proportions of water used in making the mortars was not studied. That is, the durability test was not carried out on mortars where the water-cement ratio alone varied. But as noted in the discussion of strength, those mortars requiring high amounts of water for normal flow have in the majority of cases lower strengths than those requiring the lower amounts.

It is true that producers of this commodity can point with much pride to the excellent results obtained up to the present in the matter of resistance to weathering. But too many of these cements have been on the market such a short time their true length of life has not been determined. Freezing and thawing studies should, therefore, be conducted in developing masonry cements.

The present difficulties encountered in obtaining water-tight masonry walls indicate that possibly the proper masonry cement has not yet been developed—even acknowledging that besides the cement the wall consists of a unit, the water and sand of the mortar, and the assembling of all of these. Although the linear changes found in this investigation were small relative to the total length of the specimens, field conditions seem to indicate that these changes are worthy of concern. Linear changes that may accompany the setting, hardening, and weathering are matters of consequence and producers should determine them, and how they are affected by changes in the composition of their product.

No doubt at all times the consumer will demand strength equal to or above a specified minimum. It also happens that a strength higher than the minimum of a specification is frequently used as a sales argument and accepted as evidence of an enhanced quality. The producer, therefore, is always interested in strength, but he should study this property in connection with all the others. Increased strength should not be obtained at the expense of such equally essential properties as workability, volume change, range of water content, water-retaining capacity, etc.

The majority of cements used in this study are commonly referred to as "waterproof". In this paper they have been referred to as containing "water-repellent additions". The amount of the total absorption on immersion in water as well as the rate of absorption indicates that the use of the word waterproof to describe the cements is incorrect, and even the adjective "water-repellent" is open to question. But these additions do serve to render the mortar water-shedding to

some degree. The use of the proper agents to secure this property is apparently justified, but the outstanding effect of their use seems to be that of a plasticizer. Without much doubt they do render a mortar more workable—nothing more than spreading such mortars with a trowel is needed to demonstrate that. Here again producers seem to use a wide variety of materials and have not studied their effect either as water-repellents or as plasticizers. This particular component of the cements should be studied thoroughly by all producers not only in regard to the two properties just cited, but also as to its effect on the mixing water requirements.

VI. SUMMARY

1. The cements included in the study may be grouped into the classifications, hydrated or hydraulic lime, natural cement, portland cement with or without admixtures, mixtures of portland cement and lime, portland and natural cements, portland cement with various unidentified materials, blast furnace slag with various additions, and 2 whose identity could not be established. About half of the cements contain water-repellent materials.

2. The amounts of the cements retained on a no. 450 sieve varied between 11.3 and 49.7 percent.

3. The rodded weights varied from 39.7 to 89.9 lb/ft^3; the loose weight from 32.5 to 80.6 lb/ft^3.

4. The bulk specific gravities of the neat cement pastes having a neat spread of 8 in. varied from 0.83 to 1.93, the lower specific gravities being due largely to the incorporation of air caused mainly by the presence of water-repellent materials in the cements. No correlation was found between time of flow in the neat spread test and any other property measured.

5. Mortars in the proportion of 1:3 cement-standard Ottawa sand by weight, 1:3 with mixed Ottawa sand by weight and by volume, as well as mortar with a constant ratio of 1:1.57 neat paste to mixed sand by volume were studied.

6. The water content required for workability as measured by the stirring resistance in the range of from 200 to 1,200 g was determined. The water content varied both in the amount required for maximum resistance and in the range of these amounts. The proportions of mixing water required to produce the minimum stirring resistance varied from 15.2 to 30 percent, for the maximum resistance from 9.2 to 24.2 percent. The smallest range in water content for a given cement between these limits of stirring resistance was 3 percent and the largest was 11 percent.

7. The water-retaining capacity was measured by subjecting the mortar for 1 and 3 min intervals to a suction equivalent to that of a brick of medium absorption. After 1 min of suction, from 53 to 98 percent of the water initially present in the mortar was retained. The least amount was retained by a cement largely portland, the greatest by a portalnd cement-hydrated lime mixture. In only 3 cases (cements nos. 5, 14, and 27) was there no more water extracted by the 3 min suction than by the 1 min suction. In all cases the mortars containing the maximum amount of mixing water lost more water than those mortars having the minimum amount of mixing water. Those cements containing large amounts of slag and those classified as largely portland cements lost a greater percentage of the mixing water than did those of the other classes.

8. The volume yield of mortar Y, proportioned on a 1:3 rodded volume basis, varied from 3.3 to 4.2 volumes per unit volume of cement. The larger volume yields were due to the larger volumes of air incorporated in the mortar, the increase in yield being nearly proportional to the amount of air retained. The greater amount of air was retained by mortars containing water-repellent cements. The greatest quantity of air contained by a mortar containing a non-water-repellent cement was 7.0 percent; only 2 of 23 mortars with water-repellent cements contained less than 8 percent air, only 6 less than 14 percent.

9. The shrinkage during the first 24 hr varied from 0.087 to 0.585 percent. There was little distinction between the water-repellent cements and the nonwater-repellent cements in the amount of shrinkage in 24 hr. The length changes during the year following were small in comparison to the first 24 hr shrinkage. The length changes in the first drying after removal from the damp closet were of about the same magnitude as the shrinkages in 1 yr air storage, namely, values ranging from 0.026 to 0.154 percent.

10. The compressive strengths showed an enormous range. For example, the 28 day strength of mortar Y varied from about 50 to 3,650 lb/in.^{2} The strengths of the 41 cements were scattered between these extreme values. Thirteen were below 300 lb/in.^{2}, 22 below 600 lb/in.^{2}

11. The modulus of rupture showed an approximate relation to the compressive strength; the 28 day modulus of rupture of mortar Y varied from 25 to 590 lb/in.^{2} The relation between modulus of rupture and compressive strength was sufficiently good to eliminate the necessity of including both tests in specification requirements.

12. Specimens of mortar Y, 28-day damp-closet storage, which failed in 10 or less cycles of freezing and thawing had compressive strengths less than 400 lb/in.^{2} Only 2 having strengths less than 400 lb/in.^{2} resisted more than 100 cycles; these 2 were made from natural cements.

13. The durability of the mortars when subjected to freezing and thawing tests could be predicted with reasonable accuracy by the time required for mortar specimens 1 by 4 by 6 in. aged 28 days to attain 90 percent of their 72-hr absorption. The mortar specimens, with one exception, that required more than 1 hr to absorb 90 percent of the water that would be absorbed in 72-hr were not disrupted by 10 cycles of freezing and thawing. It may be noted that the water-repellent cements are as a group more durable than the nonwater-repellent type. For example, of mortar X, aged 28 days, but 3 of the 23 water-repellent cements failed in 10 freezing and thawing cycles, whereas of the 17 nonwater-repellent cements, 13 failed in 10 freezing and thawing cycles.

14. The linear rise of water in the specimens also gives an indication of their durability. In 59 of 71 cases, those mortars with a rise of 2 in. in 3 hr or less failed in less than 10 freezing and thawing cycles. Of those with a 2-in. rise in 1 hr or less, all failed in 10 cycles or less.

15. Some cements did not develop efflorescence; in the others from a slight to a pronounced efflorescence was noted.

16. A discussion of some of the essentials of specifications for masonry cement is given, with suggested limits for the several tests.

WASHINGTON, September 21, 1934.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP747

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YOUNG'S MODULUS OF ELASTICITY AT SEVERAL TEMPERATURES FOR SOME REFRACTORIES OF VARYING SILICA CONTENT

By Raymond A. Heindl and William L. Pendergast

ABSTRACT

Determinations of Young's modulus of elasticity of 10 brands of fire-clay bricks (ranging in silica content from 48 to 52 percent), 2 brands of silica bricks, and an 80 percent alumina fire brick, were made at room temperature, 100, 200, 400, 500, 600, and 800° C. In a few cases determinations were made also at 300, 700, and 900° C. Six samples were tested through temperature regions of crystalline silica inversions at intervals of less than 100° C. The data show that the modulus of elasticity is affected greatly by the total silica content, modified by the form of the crystalline silica present and by the temperature. A general relation was found between modulus of elasticity, total silica, and linear thermal expansion.

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I. INTRODUCTION

It has been shown[1] that the 3 properties, modulus of elasticity, linear thermal expansion, and modulus of rupture when considered together give a fairly good measure of the resistance of heated clay

[1] F. H. Norton. J. Am. Ceramic Soc. 8,29(1925). M. C. Booze and S. M. Phelps. J. Am. Ceramic Soc. 8,361(1925). R. A. Heindl and W. L. Pendergast. BS J. Research 3,691(1929) RP114. K. Endell. Glastech. Ber. 11,178(1933). R. A. Heindl and L. E. Mong. J. Am. Ceramic Soc. 16,601(1933).

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ware to thermal shock. In a previous publication[2] it was reported that the modulus of elasticity of fire-clay brick was greater in most cases at 550° C than at 20° C and that the increase was not proportional to the value obtained at the lower temperature. Because of the large differences in percentage increase in Young's modulus of elasticity for the several brands of bricks tested at those 2 temperatures, it seemed logical to measure the modulus at several intervening temperatures in order to determine whether the changes were gradual or abrupt. At the same time some information might be gained as to the cause of such changes in the modulus of elasticity[3] which accompany increases in temperature.

II. MATERIALS

The fire-clay bricks used in this study were chosen from the 17 brands reported on in a previous publication,[4] but were received subsequent to the original shipment. The brands, 10 in number, were selected so that a series of bricks of a wide range in silica content would be included. In addition, 2 brands of silica bricks and an 80-percent alumina brick were investigated.

1. SILICA CONTENT

The bricks were analyzed for silica content by the sodium carbonate fusion method. It was the only chemical determination.[5] The fire-clay bricks ranged in silica from 47.8 to 81.9 percent. The silica bricks contained 96 percent silica and the high alumina brick 15.7 percent.

2. PYROMETRIC CONE EQUIVALENTS

The pyrometric cone equivalents (pce or softening points) were determined according to the ASTM standard method, serial designation C 24–33.[6] The values, which are given in table 1, were included to indicate that, with one exception (brand J), the materials were of a grade of refractoriness that would preclude the formation of appreciable quantities of glass when reheated at 1,400° C for 5 hours. Eight of the 10 fire-clay brick have a pce of 31 or above.

[2] R. A. Heindl and W. L. Pendergast. BS J. Research **3**,691(1929) RP114.

[3] The results of similar studies of the elastic properties of ceramic bodies have been given in the following reports: R. Rieke and S. Muller, *The elasticity and plastic softening of some sagger clays and of porcelain.* Ber. Deut. Keram. Ges. **12**,419(1931). K. Endell and W. Mullensiefen, *On the elastic distortion and plastic deformation of refractory bricks at 20° and at higher temperatures.* Ber. Deut. Keram. Ges. **14**,16(1933). A. L. Roberts and J. W. Cobb, *Behavior of refractories under torsion at different temperatures.* Trans. Ceramic Soc. **32**(1933).

[4] See footnote 1, p. 851.

[5] Made by E. H. Hamilton of the Bureau staff.

[6] American Society for Testing Materials Book of Standards for 1933, pt. 2, p. 184.

TABLE 1.—*Silica content and some properties of the refractories*

TABLE 1.—*Silica content and some properties of the refractories*

Brand [1]	Silica content [2]	pce [5]	Tested as received from manufacturer									Tested after reheating for 5 hours at 1,400° C							
			Porosity	Young's modulus of elasticity (1,000 lb/in.²) at—								Porosity	Young's modulus of elasticity (1,000 lb/in.²) at—						
				20° C	100° C	200° C	400° C	500° C			800° C	900° C		20° C	100° C	200° C	400° C	500° C	600° C	700° C	800° C
	Percent	*Cone no.*	*Percent*										*Percent*								
Q	47.8	33	15.2	1,990	1,960	2,120	2,220	2,210	2,270	2,100	1,075	770	14.5	2,920	2,890	2,910	2,880	2,990	3,040	3,150	1,510
C	51.1	33	20.5	680	710	890	1,050	1,220	1,270	------	950	------	20.0	1,830	1,895	2,045	2,240	2,260	2,360	------	2,020
B	53.6	32	21.9	1,550	1,800	2,020	2,050	2,410	2,600	------	2,360	1,140	20.4	3,860	4,290	4,620	5,080	5,250	5,570	4,715	4,170
R	55.5	32 to 33	23.0	3,410	3,000	3,600	3,920	4,260	4,760	4,720	4,050	------	21.9	3,610	3,800	4,400	4,690	5,470	6,200	------	4,960
E	55.2	32 to 33	16.5	1,570	1,560	1,640	1,940	2,060	2,210	2,190	2,070	1,280	15.6	3,580	3,820	4,200	4,500	4,630	4,660	------	4,270
I	56.7	31	24.0	580	570	610	720	770	950	------	940	------	18.8	2,510	2,540	2,680	2,980	3,270	3,510	------	2,230
J	60.3	28 to 29	13.1	2,560	2,590	2,740	2,930	3,120	3,620	------	3,040	------	9.6	5,820	5,850	5,960	6,300	6,740	6,050	------	4,450
G	66.6	32 to 33	31.4	990	940	1,120	1,260	1,420	2,240	2,400	2,130	1,690	29.0	1,360	1,340	1,360	1,770	2,020	2,800	3,170	2,980
P	69.7	30 to 31	26.6	1,520	1,410	1,530	1,890	2,180	3,400	------	3,080	------	23.9	2,300	2,190	2,340	3,270	3,920	4,860	5,175	5,040
H	81.9	31	30.3	350	360	365	495	645	1,380	1,630	1,410	------	30.4	390	340	355	570	680	1,390	1,660	1,520
X [3]	96.3	32	32.4	1,060	830	630	1,300	1,990	2,270	2,070	1,620	------	------	------	------	------	------	------	------	------	------
Y [3]	96.0	32 to 33	28.9	450	400	330	590	770	1,040	1,320	970	------	------	------	------	------	------	------	------	------	------
Z [4]	15.7	Over 37	38.8	2,700	2,700	2,770	2,800	3,030	3,335	3,100	2,270	------	------	------	------	------	------	------	------	------	------

[1] Key letters of fire-clay brick correspond to those referred to in BS Research Pap. RP114.
[2] The silica content of the 80 percent alumina brick was furnished by the manufacturer of the brick.
[3] Silica brick, modulus of elasticity values (lb/in.²) at:

	160° C	300° C	550° C	650° C
(X)	510, 000	950, 000	2, 140, 000	------
(Y)	340, 000	470, 000	890, 000	1, 280, 000

[4] High alumina brick.
[5] Pyrometric cone equivalent.

3. POROSITY

The procedure for making the porosity determinations was as follows. Three specimens, 1 by 1 by 2 inches, of each brick were saturated by boiling them in water for 2 hours and allowing them to cool in the water overnight. The porosity was taken as the ratio of the volume of water absorbed to the bulk volume of the specimen.

The porosities are given in table 1, both for the bricks as received from the manufacturer and after reheating in a laboratory furnace at 1,400° C for 5 hours. The values for the fire-clay bricks range from 13.1 to 31.4 percent for the samples as received and from 9.6 to 30.4 percent for the same samples after reheating. It is evident that in the majority of cases the reheating does not appreciably affect the porosity.

III. METHODS OF TESTING

1. LINEAR THERMAL EXPANSION

The data on linear thermal expansion (figs. 2 and 3) were taken, with 2 exceptions (brands G and H), from the report previously cited.[7] Specimens approximately ⅞ by ⅞ by 6 inches were used for the tests, which were made as described in that report.

2. YOUNG'S MODULUS OF ELASTICITY

The apparatus used and the method for determining Young's modulus of elasticity have been described in other publications.[8] However, a change was made from wire-resistance units to recrystallized silicon carbide units for heating the furnace. In making this change the interior dimensions of the furnace were not affected, but additional insulating material was placed in the walls. The apparatus and rebuilt furnace are shown in figure 1.

One brick of each brand was cut into specimens 1 by 1 by 9 inches, and 2 or more from each brick were tested in flexure as received from the manufacturer and also after having been reheated at 1,400° C for 5 hours in a laboratory furnace. Tests were made at the following temperatures: room (approximately 20° C), 100, 200, 400, 500, 600, and 800° C. A few specimens were also tested at 300, 700, and 900° C. The results are given in table 1. One specimen each of 6 brands was tested at intervals of less than 100° C through the temperature regions of crystalline silica inversions.

IV. RESULTS AND DISCUSSION

1. EFFECTS OF REHEATING AND OF VARIOUS TEMPERATURES ON YOUNG'S MODULUS OF ELASTICITY

In figures 2 and 3 each group of curves refers to an individual specimen. Comparison of the dotted and solid curves shows the changes which have taken place in the elasticity of the bricks due to the reheat treatment. The elasticities, expressed as moduli, determined at the various temperatures of test are plotted in the figures as open circles. Figure 2 shows the values for those bricks which after reheating have a maximum modulus of elasticity below 3,500,000 lb/in.^{2} and

[7] R. A. Heindl and W. L. Pendergast, BS J. Research **3**,691(1929)RP114.
[8] R. A. Heindl and W. L. Pendergast, BS J. Research **3**,691(1929)RP114. J. Am. Ceramic Soc. **10**,524 (1927).

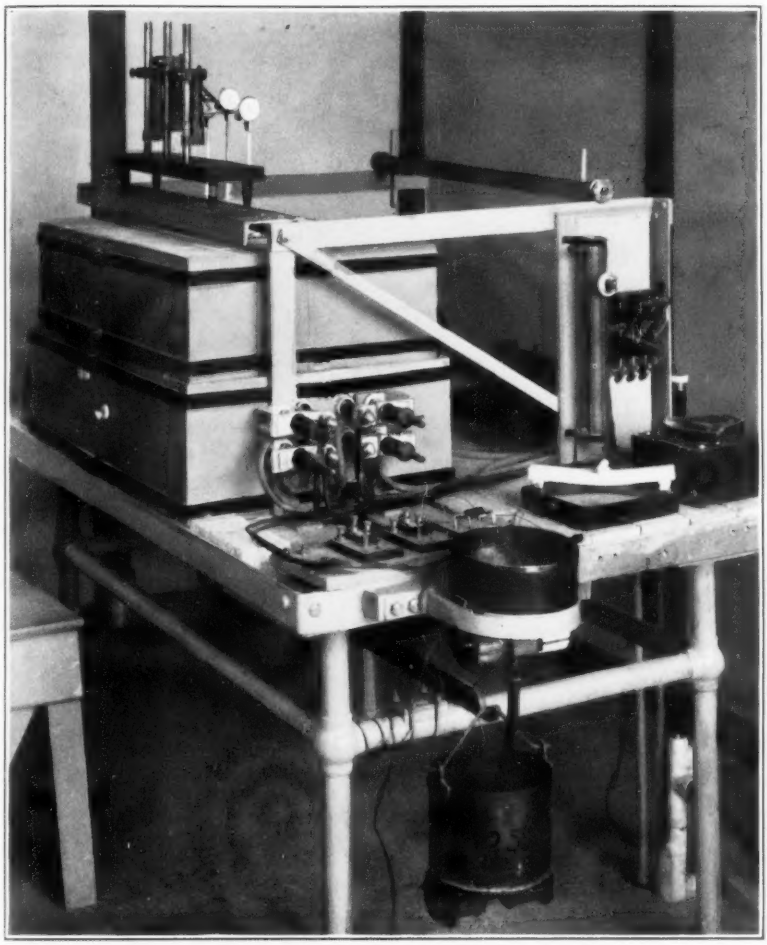

FIGURE 1.—*Furnace and equipment used in determining Young's modulus of elasticity of refractory brick by flexure tests.*

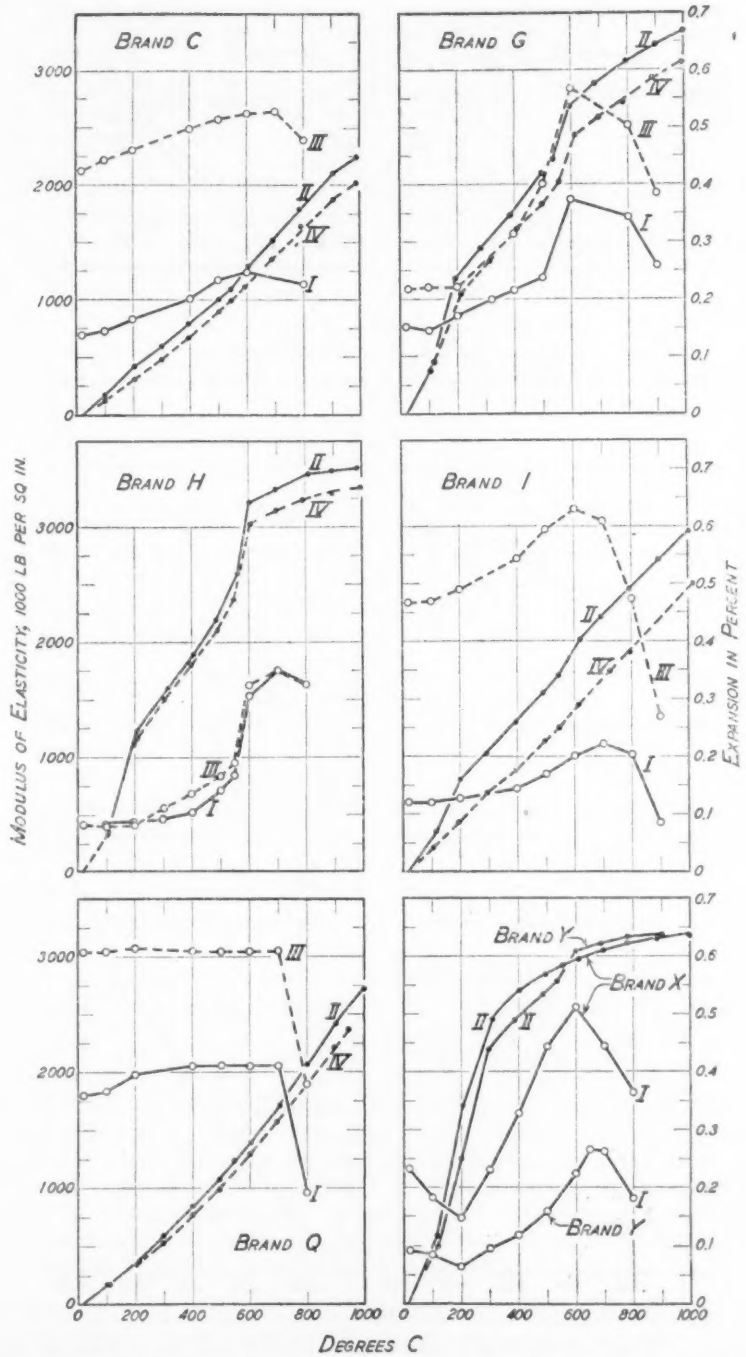

FIGURE 2.—*Young's modulus of elasticity (open circles), and linear thermal expansion (solid circles), of specimens cut from refractory brick.*

Values for a series of different temperatures are given as obtained on the material received from the manufacturer (identified by I and II) and also after reheating in laboratory furnaces at 1,400° C (identified by III and IV).

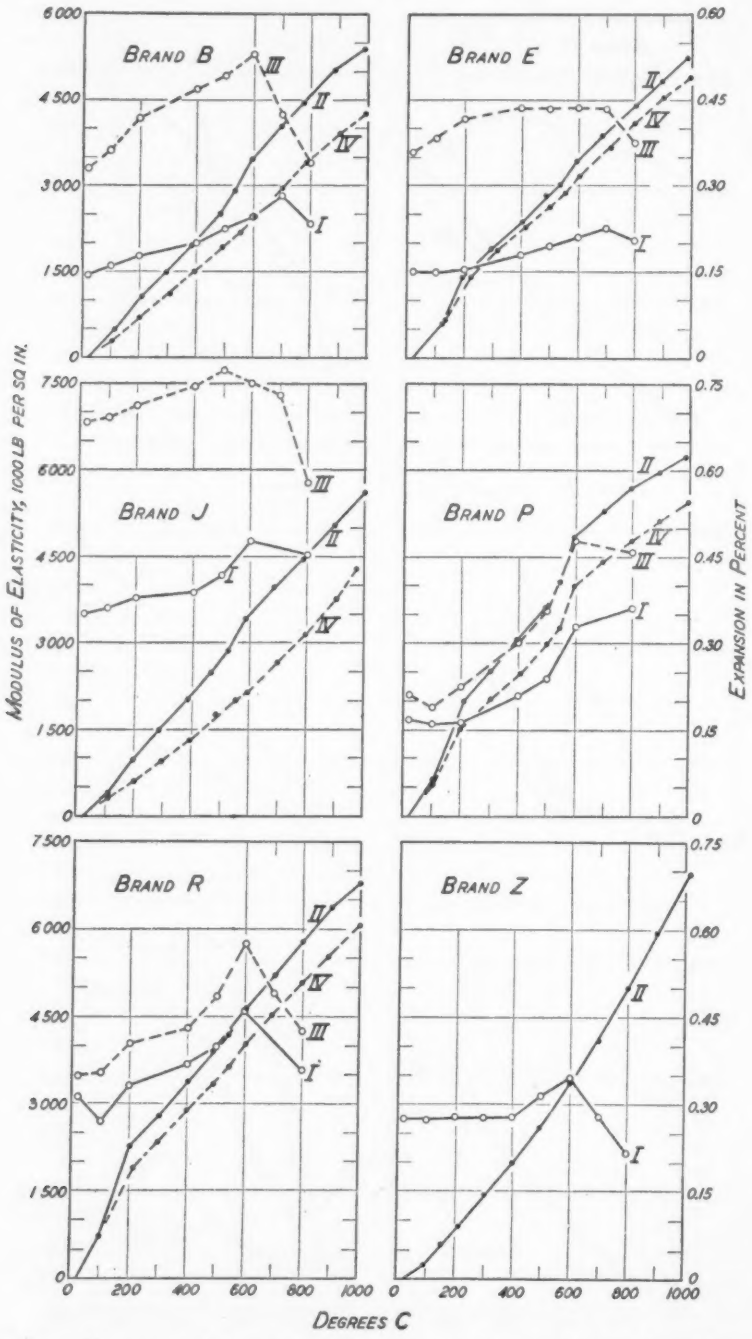

FIGURE 3.—*Young's modulus of elasticity (open circles), and linear thermal expansion (solid circles), of specimens cut from 5 brands of refractory brick and 2 brands of silica brick.*

Values are given as obtained at a series of different temperatures on material as received from the manufacturer (identified by I and II) and also after heating in laboratory furnaces at 1,400° C (identified by III and IV).

the values in figure 3 are for bricks having a maximum modulus above 3,500,000 lb/in.[2] The corresponding linear thermal expansions are plotted as solid circles (scale at the right) for each of the bricks to show conveniently whether or not crystalline silica is present in appreciable quantities.

Although the lines connecting the values of the modulus of elasticity, obtained at the various temperatures, are in general parallel for the reheated and nonreheated specimens (figures 2 and 3), it is evident that the reheating in most cases did increase greatly the values for any one temperature.[9]

It was found that the modulus of elasticity of each of the 2 brands of silica bricks and also that of brands H (reheated), P and R (non-

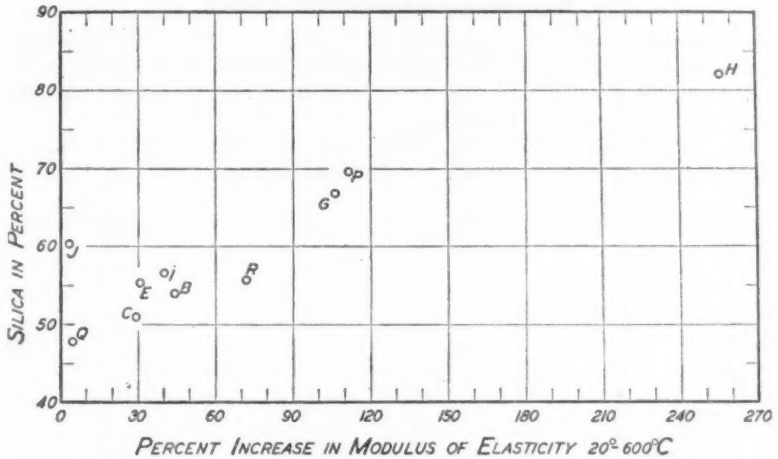

FIGURE 4.—*Relation between the percentage change in Young's modulus of elasticity for the temperature range 20 to 600° C and the silica content of fire-clay brick.*

reheated) was slightly lower at 100° C than at 20° C, and in every case the maximum modulus of the refractories was found at, or below, 700° C.

In general, the figures show that the modulus of elasticity for brand Q remained practically constant between 20 and 700° C; for brands G, H, J, P, and R the increase in the modulus was small but gradual between 20 and 500° C and rather large between 500 and 600° C; for brands B, C, E, and I the increase was gradual between 20 and 600° C. For the silica bricks the modulus decreased sharply between 20 and 200° C and increased fairly uniformly and rapidly between 200 and 600° C while, for the high alumina brick, the values remained constant to about 400° C and then increased uniformly to 600° C. It may be seen in most cases that the irregularities in the lines connecting the values of the modulus correspond to the temperature ranges in which inversions of crystalline silica take place.

[9] It was pointed out that the porosity of the bricks was not greatly affected by the reheat treatment. It follows that the porosity cannot be relied upon to give any information of such changes in elasticity. Furthermore, the porosity bears no apparent relation to the modulus of elasticity of bricks of approximately the same pce values.

2. RELATION OF MODULUS OF ELASTICITY TO SILICA CONTENT AND TO LINEAR THERMAL EXPANSION

(a) SILICA CONTENT

Figure 4 shows a relation between silica content and percentage change in modulus of elasticity from room temperature to 600° C as calculated from those values in table 1, which were obtained on the specimens reheated at 1,400° C. However, such a relation is apparently found only when bricks of approximately the same refractoriness are compared, since an exception to the relation is brought out in the case of brand J, which has a pce of only 28–29. A similar relation was noted for the samples tested as received.

(b) LINEAR THERMAL EXPANSION

A comparison of the expansion curves in figures 2 and 3 with the lines connecting the modulus of elasticity values shows that either a decrease or practically no change in modulus accompanied the inversion of tridymite and cristobalite.

The curves show further, with one exception (brand R), that wherever the rate of expansion increased between 500 and 600° C.,

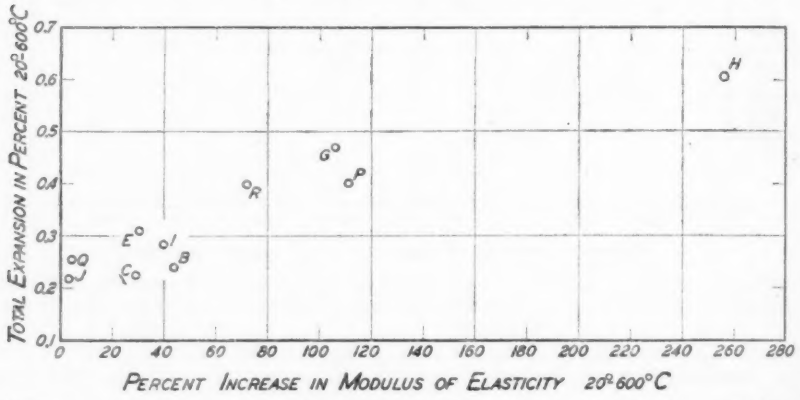

FIGURE 5.—*Relation between the total percentage change in Young's modulus of elasticity of fire-clay brick for the temperature range 20 to 600° C and the total percentage linear thermal expansion for the same range.*

caused by the inversion of alpha to beta quartz, there was also a large increase in modulus of elasticity. (For instance, in the case of specimen H the increase amounted to about 115 percent.) Petrographic examination of brick of brand R, which showed an appreciable increase in modulus of elasticity between 500 and 600° C, indicated a noticeable quantity of quartz even though the expansion curve failed to show its presence.[10]

The total linear thermal expansions, from room temperature to 600° C of the fire-clay bricks after having been reheated are plotted in figure 5 against the percentage change in modulus of elasticity for the same range in temperature. Changes in modulus of elasticity were based on the values given in table 1 and the expansions were taken from the curves in figures 2 and 3. It will be noted that a fairly consistent and approximately linear relation exists between the percentage change in elasticity and expansion of fire-clay brick.

[10] A similar phenomenon has been observed by J. B. Austin and R. H. H. Pierce, Jr. J. Am. Ceramic Soc. **16**,104 (1933); and by R. G. Geller, D. N. Evans, and A. S. Creamer, BS J. Research **11**,327 (1933) RP594.

3. EFFECT OF MODIFICATIONS OF UNCOMBINED SILICA ON MODULUS OF ELASTICITY

The trend of certain curves established by modulus determinations at 100° intervals indicated that significant changes in modulus might be established by making tests at smaller intervals, more particularly

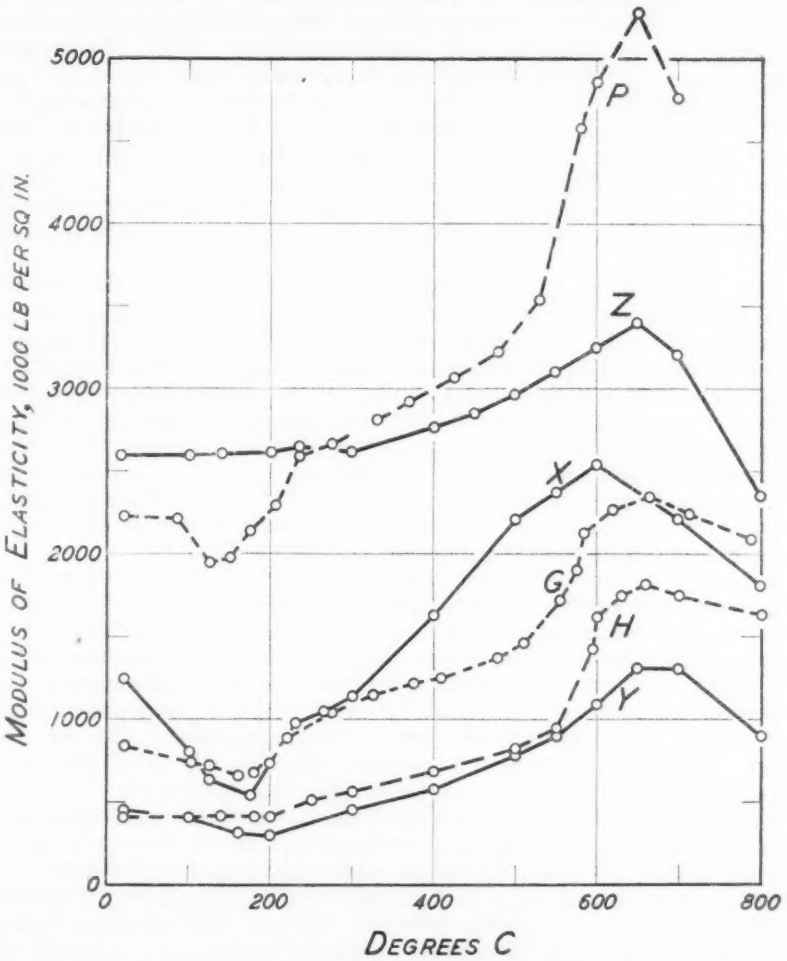

FIGURE 6.—*Young's modulus of elasticity of specimens cut from 6 brands of refractory brick.*

Values are given for intervals of less than 100° C through critical temperature ranges. Data on silica bricks X and Y and high alumina brick Z were obtained on the specimens as received from the manufacturer, and data on fire-clay bricks G, H, and P after the specimens had been reheated at 1,400° C for 5 hours.

with regard to changes in modulus which might accompany the large volume changes caused by the inversions of crystalline silica. Some measurements were, therefore, made at intervals of less than 100° C on 1 specimen each of fire-clay bricks of brands G, H, and P, 2 brands of silica bricks and the high alumina brick. The results [11] are shown

[11] Because it was necessary to use different specimens in these tests from those used for obtaining the results plotted in figures 2 and 3, the results do not necessarily check. This is illustrated by the values for the 3 specimens of a brick of brand H, table 2.

in figure 6. The modulus of elasticity for fire-clay bricks P and G and silica bricks X and Y was appreciably lower within the tridymite inversion temperature range (150 to 175° C) than at room temperature. The modulus for specimens of G, P, and X shows a marked increase between 175 and 230° C, which is within the temperature range of the cristobalite inversion; and those for specimens G, H, and P show a marked increase between 500 and 600° C, which covers the range of the alpha to beta quartz inversion. Each of the specimens shows a uniform increase in modulus between about 250 and 550° C, and the maximum modulus was reached at approximately 650° C. Although the high alumina brick Z and the highly siliceous brick H approximate extremes in composition, the modulus in both cases show little difference in trend between 20 and 550° C. At the latter temperature the modulus for Z continued to increase uniformly to 650° C, whereas the modulus for H increased markedly to about 600° C.

No quantitative petrographic tests were made of the relative quantities of quartz and cristobalite, but an estimate indicated specimen G contained about 3 times as much quartz as cristobalite; H contained less than half quartz, approximately one-third cristobalite and apparently no tridymite; P contained somewhat more quartz than cristobalite and tridymite combined; and R contained only a small percentage of quartz in comparison to the cristobalite. Silica brick X contained very little quartz and glass, and large amounts of cristobalite and tridymite with the latter in preponderance. Silica brick Y contained possibly as much as 25 percent quartz and noticeably less tridymite than specimen X.

Although in the case of the specimens G, P, X, and Y the modulus decreased noticeably between approximately 100 and 200° C, in no case was the value at 600° C lower than the value at 550° C. It would appear that the decrease in the modulus between approximately 100 and 200° C in these specimens is caused by the presence of considerable quantities of tridymite since very little decrease was observed in brick H, which apparently contained no tridymite. On the other hand, the great increase in modulus between 550 and 600° C is apparently caused by the presence of crystalline quartz.

The silica content of the 2 silica bricks is identical, yet differences in structure and mineralogical composition result in the 2 brands having quite different moduli at corresponding temperatures. As previously stated, silica brick X, which showed a much larger decrease in the modulus of elasticity between 100 and 200° C than Y, contained noticeably more tridymite.

4. EFFECT OF SLOW COOLING AND QUENCHING ON MODULUS OF ELASTICITY

When attempting to obtain check results by making duplicate measurements on a specimen that had been tested through the range of temperatures outlined it was noted that the values were lower than those obtained in the first test. It was believed that the slow cooling or perhaps partial annealing treatment of the specimens was responsible for the change. Table 2 gives the results obtained on a few samples of bricks before and after slow cooling from 800° C. In addition, some of the specimens were quenched in air from 800 and 1,000° C to determine whether or not strains would be set up by the

TABLE 2.—*Modulus of elasticity of refractory brick at room temperature. Showing effect of slow cooling versus quenching*

Brand	Young's modulus of elasticity (1,000 lb/in.²)				
	Original test	Tested after—			
		Slow cooling from 800° C	Quenching in air from 800° C	First quenching in air from 1,000° C	Second quenching in air from 1,000° C
P	2,220	1,810	1,460	1,220	1,160
X	1,155	750	780	990	1,030
Y	450	240	----	300	----
Z	2,790	2,550	----	2,720	----
Ha	560	350	----	----	----
Hb	400	270	----	210	170
Hc	290	220	----	160	80

rapid cooling treatment. It is interesting to note that the modulus of elasticity of the silica bricks X and Y increased with the quenching treatment and that the modulus of elasticity of the siliceous brick (P and H) continued to decrease. Within limits, such a decrease is believed to be beneficial with respect to increased resistance to thermal shock. Although the modulus of the high alumina brick Z also increased with the quenching treatment, the change was not appreciable.

V. SUMMARY AND CONCLUSIONS

Ten brands of fire-clay bricks covering a wide range in silica content (48 to 82 percent silica); 2 brands of silica bricks (96 percent silica); and 1 of high alumina bricks (16 percent silica), were selected and Young's modulus of elasticity determined for each. The fire-clay bricks were tested as received from the manufacturer and also after reheating in a laboratory furnace at 1,400° C for 5 hours. The effect on the modulus of elasticity of the pce and porosity and the form or forms of uncombined silica was also studied.

After testing the bricks at 20, 100, 200, 400, 500, and 600° C, it was found that, with one exception, the modulus of elasticity was affected significantly by the temperature. For 5 brands of fire-clay bricks the modulus increased gradually between 20 and 500° C and rather abruptly between 500 and 600° C; for 4 other brands of fire-clay bricks the increase was gradual between 20 and 600° C; for the 2 brands of silica bricks the modulus decreased from 20 to 175° C and increased from 175 to 600° C. The decrease of the modulus in the lower temperature range was noted also in highly siliceous fire-clay bricks. The modulus of the high alumina brick remained constant to 400° C, then increased gradually to 600° C.

There is a fairly consistent and approximately linear relation between percentage increase in modulus of elasticity between room temperature and 600° C and the silica content, and also the total linear thermal expansion, provided the bricks are of approximately the same refractoriness and have not been heated sufficiently high to dissolve the silica.

On testing 2 silica bricks and 3 highly siliceous fire-clay bricks at temperature intervals of less than 100° C, it was found (except for 1

fire-clay brick) that the modulus of elasticity decreased at the approximate temperature of inversion of tridymite, increased at the approximate temperature of inversion of cristobalite and that, in every case, the inversion of quartz caused an increase.

Several specimens were tested before and after having been cooled comparatively slowly from 800° C. Results indicated that the modulus of elasticity was lowered by this treatment. On the other hand when the specimens were air-quenched from 800 and 1,000° C, the modulus of elasticity was decreased for the fire-clay bricks, increased for the silica, and the change in high alumina brick was practically negligible.

WASHINGTON, October 3, 1934.

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COMPARISON OF THE GROUND-PLANE AND IMAGE METHODS FOR REPRESENTING GROUND EFFECT IN TESTS ON VEHICLE MODELS

By Roy H. Heald

ABSTRACT

In order to simulate full-scale conditions when vehicle models are tested in the wind tunnel it is necessary to represent the presence of the ground. Approximate representation of ground effect can be obtained by means of either the fixed ground-plane method or the image method. An experimental comparison of the two methods, in which concordant results were obtained, is described and the results are discussed from the viewpoint of present knowledge of air flow.

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I. INTRODUCTION

Two methods for investigating the air resistance of vehicles have become established. The more direct one is by means of road tests, using full-scale equipment, but because of the expense involved and the difficulty of securing accurate comparative data, this method appears better suited for final performance tests. The wind-tunnel method, using models, while less direct has the advantage of convenience and comparatively low cost, both items of some importance if it is desired to conduct a systematic study of the air forces on a considerable number of body forms. While the use of the results of wind-tunnel tests for estimating full-scale forces is not entirely satisfactory because of the lack of precise knowledge of the effect of the scale of the model and the effect of turbulence in the wind tunnel, the results do constitute valuable guides in design.

The early use of wind-tunnel measurements on models as a basis for estimating the air forces acting on moving vehicles is associated with the experiments conducted by Goss and Solberg [1] on models of

[1] Proc. Western Ry. Club **10**, 347 (1898).

railroad trains. More recent investigations, particularly those dealing with the development of new body shapes for automobiles, also have been confined largely to wind-tunnel experiments. One of the problems arising in this connection is that of representing the effect of the presence of the ground on the air resistance of a moving vehicle.

While the possibility of the effect of aerodynamic interference between a moving vehicle and the ground has been recognized, no sound and practical method for its evaluation in the wind tunnel has been given. The problem is one of relative motion. When a vehicle is driven in still air, the relative motion between the ground and the surrounding air is zero; the motion of the full-scale vehicle is therefore with respect to both the ground and the air. In the wind tunnel the air moves with respect to both the model and the ground plane. Thus the wind-tunnel arrangement represents actually only the condition when the vehicle is stationary and a horizontal wind blows against it. A closer approximation of the actual conditions is obtainable by means of a belt moving close beneath the model in the wind tunnel, its linear velocity being adjusted so that the relative motions of the air stream, the model, and the belt simulate full-scale conditions. The mechanical difficulties inherent in this method of representing the ground effect are numerous and consequently some more easily used method has been sought.

The method of images, described by Rumpler,[2] is designed to replace the direct representation of ground effect in the wind tunnel. As implied by the title it involves measurement of the air force on duplicate models, one inverted, fastened wheel to wheel. See figure 1 (B) and (C). The drag of the pair is determined and one-half the net drag is taken to represent the drag of one model. This method is dependent on the assumption that the laws of air flow apply in precisely the same way to the duplicate model set-up as to the actual vehicle moving along the ground, an assumption whose validity is not established. The experimental background is made up of the results of some investigations in which, to a large extent, the model and full-scale measurements are uncorrelated. The conclusion to be drawn from a study of available data is that the full-scale forces are of the order of magnitude to be expected from model tests but the comparisons are uncertain, because of the probable effects of Reynolds number and wind-tunnel turbulence.

In an extensive investigation, the construction of accurate models in duplicate is tedious and costly. Both time and expense can be saved by the use of a single model. Hence the ground-plane method, which consists in testing one model close to a large stationary platform in the wind tunnel, has come into use. The results obtained by either of the methods must be regarded as comparative only, since neither method has been shown to be an exact representation of actual conditions.

A few experimental comparisons which show good agreement between the ground-plane and image methods have been made. Others indicate decided lack of agreement. Consideration of the results of recent investigations, among them the work of Hansen,[3]

[2] Zeit. f. Flug. u. Motorluft. **15**, 22 (1924).
[3] Nat. Adv. Comm. Aeron. (October 1930), Tech. Memo. 585.

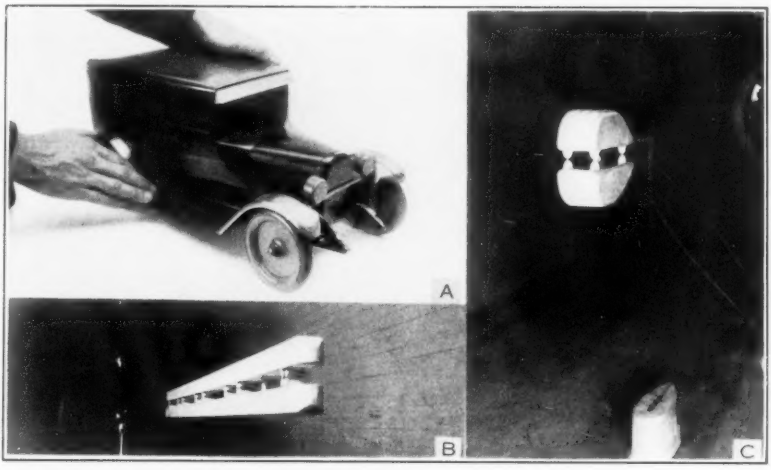

FIGURE 1.—*Views of the models used for comparing the image and ground-plane methods.*

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concerning the velocity distribution in the boundary layer [4] of a flat plate, led to the belief that the discordance might be ascribed to an effect of the shape of the leading edge of the platform in the case of the ground-plane method.

II. EXPERIMENTAL COMPARISON OF THE IMAGE AND GROUND-PLANE METHODS

It appeared desirable to investigate the effect of the shape of the leading edge of the ground plane on the results of drag measurements and to compare the image and ground-plane methods. For this purpose two types of models were constructed, one representing in general proportions a railroad train, the other a streamline automobile.[5] Views of the models arranged for tests using the image method are shown in figure 1 (B) and (C). In some earlier experiments a model of a conventional automobile, shown in figure 1 (A), was used. In addition to measurements of drag, the speed distribution near the ground plane was measured for two types of leading edge.

1. EXPERIMENTAL PROCEDURE

The arrangement of the apparatus for measuring the air resistance of the train and streamline automobile model is shown in figure 2.

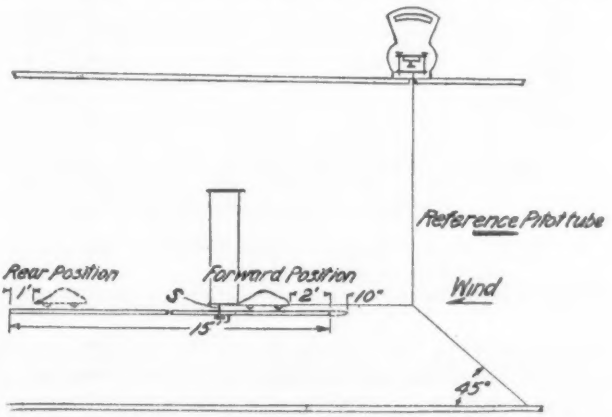

FIGURE 2.—*Arrangement of apparatus used for the ground-plane method.*

The platform was 8½ feet wide extending completely across the wind tunnel. Its upper surface was 2½ feet above the floor of the wind tunnel.

The automobile models were supported by vertical steel wires having a diameter of 0.0085 inch; the train models by wires of diameter 0.02 inch. A single fine wire extended horizontally, from the nose of the

[4] The distribution of velocity in the boundary layer (before separation) of a body moving with uniform velocity in still air can be visualized as follows: At the surface of the body the air is at rest with respect to the body. A short distance out from the surface the velocity is finite although small. As the distance from the surface increases the velocity with respect to the body increases until it becomes equal to the velocity of the body with respect to the ground, i. e., the air is undisturbed and is stationary with respect to the ground. The boundary layer has no definite limit. Its thickness may be defined as the distance from the surface required for the velocity to reach 99 percent of free stream velocity. On the basis of this definition the thickness, δ, in feet, of the boundary layer at a distance, x feet, from the sharpened leading edge of a flat plate is: $\delta = 4.8\sqrt{\frac{x\nu}{V}}$, where $\nu = 0.00016$ ft^2/sec at 15° C, 760 mm Hg and V is the velocity in feet per second.

[5] As shown in figure 1 (B) and (C), these models resembled actual vehicles only in general shape. They were constructed for the particular purpose of comparing the 2 methods of representing ground effect for different body types.

model to a point some 10 feet upstream, where it formed a junction with a 45-degree wire and a vertical wire running to the yoke on the balance. This arrangement gives equal tensions in the vertical and the 45-degree wires when a drag force is applied to the model. The model was maintained in a fixed position by means of an adjustable yoke mounted on the platform of a balance above the tunnel. The yoke being capable of fine adjustment, it was possible by focusing a telescope on a reference point on the model, to maintain the original position, very closely, during the taking of observations.

The two types of leading edge shown in figure 3, were used in the experiments by the ground-plane method. Some measurements were made on the train and streamline automobile models at several different distances above the ground plane. In the case of the automobile model, drag measurements were made also for positions near the leading and trailing edges of the platform using the faired leading

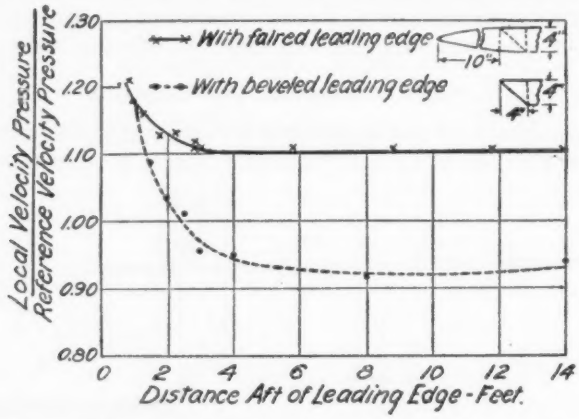

FIGURE 3.—*Results of traverse along a median horizontal line, 3 inches above the ground plane.*

The excess of the local velocity pressure over the reference velocity pressure results from the blocking effect of the platform and support.

edge. Velocity surveys were made above the platform in the vertical median plane, using both the beveled and faired leading edges, the pressures being measured by means of a Pitot-static tube and referred to the pressure readings of a reference Pitot-static tube mounted on a projecting strut above and some 2 feet ahead of the platform.

In the experiments by the image method, a housed counterweight was suspended by a small vertical wire several feet below the models; otherwise the suspension was similar to that used with the ground plane. The drag of this wire and the drag of 4 small pins (diameter, 0.10 inch) which served to hold the models together was computed and deducted from the total observed drag, leaving the drag of 2 models, 2 stings, and 8 wires. A small correction also was necessary for the drag of the counterweight spindle S, figure 2, in the case of ground-plane method. Pressure drop corrections were not applied.[6]

[6] The pressure drop or buoyancy correction is sometimes applied to the results of drag measurements of models. The correction is based on the drop in static pressure in the part of the tunnel where the model measurements are made. If the model drag is measured in pounds, the pressure drop correction, in pounds, assuming a uniform pressure gradient, is given by the formula $(p_1-p_2)\frac{C}{l}$, where p_1 and p_2 are the pressure at the front and rear of the model position in feet of water. C and l are respectively, the volume, in cubic feet, and the length, in feet, of the model. The correction is subtractive, but in the case of short models is usually so small that it can be neglected.

2. RESULTS

(a) VELOCITY PRESSURE MEASUREMENTS

The results of the velocity pressure survey are plotted in figures 3 and 4. Figure 3 refers to a median horizontal line 3 inches above the platform extending from leading edge to trailing edge; figure 4 to a vertical line 2 feet downstream from the leading edge. It will be seen that the shape of the leading edge exerts a substantial influence on the velocity distribution in the neighborhood of the platform. Although the curves are nearly coincident for a position 1 foot downstream from each leading edge, the curve for the beveled edge shows a more rapid decrease in velocity as the trailing edge is approached. The faired leading edge gave rise to substantially uniform velocity in the 3-inch horizontal pane, beginning about 3 feet back from the leading edge.

The difference is shown more clearly, figure 4, in the traverse along a vertical line 2 feet aft of the leading edge. The beveled leading edge

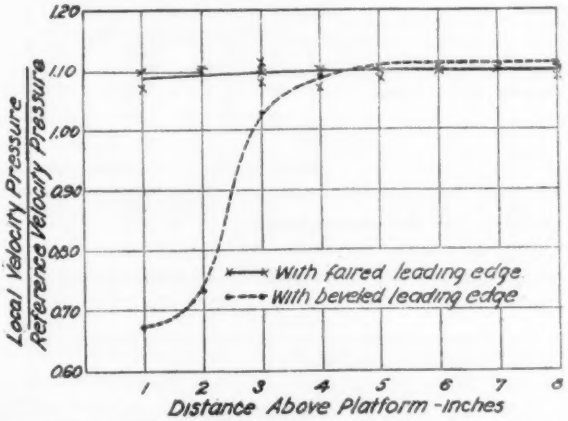

FIGURE 4.—*Results of traverse along a vertical line 2 feet aft of the leading edge of the ground plane.*

The excess of the local velocity pressure over the reference velocity pressure at some distance from the ground plane is due to the blocking effect of the platform and support.

caused a rapid decrease in velocity pressure, beginning about 4 inches above the surface of the platform. One inch above the platform the local velocity pressure was found to be about two-thirds of the velocity pressure in the free stream. With the faired leading edge on the other hand, there was little decrease at the 1-inch station. The theoretical thickness of the boundary layer for a thin plate is about 1.3 inch for the average speed (60 ft/sec) at which the traverses were made.

(b) DRAG MEASUREMENTS

The results of the drag measurements are given in tables 1 to 3. Tables 1 and 2 give the results of the comparison using the streamline automobile models, table 1 being a sample summary sheet. In these 2 tables, one-half the drag of the 2 models and the support system, as determined by the image method, is compared with the drag of 1 model and its support system, as determined by the ground-plane

method. The observed values of the total drag for several speeds were divided by the square of the corresponding speeds and the mean values of this ratio together with the mean deviations are given in table 2. The use of a ratio based on total drag eliminates the errors arising from the determination of support correction.

TABLE 1.—*Summary sheet of tests on streamline automobile models*

Figure 1 (C)

Method	Air speed [a] mph V	Total drag	Corrections	Drag of 1 model 4 wires and sting D	$\frac{D}{V^2}$
		Pounds			
Ground-plane method.—Platform with faired leading edge. Forward position of model. Wheels 1/16 inch above platform.	54.3	0.312	[b] 0.009	0.303	0.000103
	55.4	.326	.009	.317	103
	56.6	.332	.009	.323	101
	57.8	.346	.010	.336	101
	58.9	.356	.010	.346	100
Mean					[d] 0.000102
Image method.—Models suspended 3½ feet above platform, 1/8-inch space between wheels.	54.8	0.654	[c] 0.020	0.317	0.000106
	56.1	.674	.021	.327	104
	57.1	.702	.022	.340	104
	58.4	.731	.023	.354	104
	59.5	.752	.023	.365	103
Mean					[e] 0.000104

[a] Speed in the free stream 2 feet ahead of the model.
[b] Computed for counterweight spindle.
[c] Computed for holding pins and counterweight wire.
[d] Mean deviation 1.2 percent.
[e] Mean deviation 0.6 percent.

TABLE 2.—$\frac{D}{V^2}$ *for streamline automobile models* [a]

Figure 1 (C)

Wheel clearance	Ground-plane method			Image method	1 model at center of tunnel, i. e., ground not represented
	Faired leading edge		Beveled leading edge		
	Forward position	Rear position	Forward position		
Inch					
1/16	0.000102±1.2%	0.000104±0.2%	0.000095±0.4%	0.000104±0.6%	0.000115±1.0%
5/16	0.000103±0.7%	0.000101±1.0%	0.000090±0.4%	0.000104±1.0%	----------
9/16	0.000106±0.6%	0.000096±0.4%	0.000091±0.8%	0.000104±0.6%	----------

[a] D refers to drag of 1 model, the sting and 4 wires. Mean value $\frac{\text{Drag of support system}}{V^2}$=0.000039. Projected frontal area of 1 model=0.0975 sq ft.

TABLE 3.—$\frac{D}{V^2}$ *for conventional automobile model* [a]

Figure 1 (A)

Wheel clearance	Ground-plane method	Image method
1/16 inch...	0.000728±1.8%	0.000744±0.7%

[a] D refers to net drag of one model. Projected frontal area of one model=0.393 sq ft.

The results for the ground plane with faired leading edge show good agreement with those obtained by the image method for both forward and rear positions. With the model in the forward position above the ground plane and with the beveled leading edge in place, the values of $\frac{D}{V^2}$ obtained by the ground-plane and the image methods differed by some 12 percent. When the drag of the support wires was subtracted, the divergence was of the order of 22 percent of the net drag of the model. This discordance is not surprising in view of the results of the velocity survey above the ground plane, since the shape of the leading edge was found to exercise a marked effect on the thickness of, and the velocity distribution in, the boundary layer of the ground plane. The results of this part of the investigation indicate that the shape of the leading edge of the ground plane is an important factor in determining the drag of a faired model tested near the plane.

The effect of raising the model slightly above the platform, i. e., of wheel clearance, was found to be small, presumably because of the fact that the body proper, even in the nearest position, was separated from the platform by an amount slightly greater than the wheel radius, and hence was largely out of the region of low-speed air.

The results of the earlier comparative tests on a model of a conventional automobile (figure 1 (A)) are given in table 3. In this case the model was suspended by four wires arranged in V's at the front and rear, the total drag being computed from the observed displacement of the model due to the wind, the swinging radius, and the weight. Although this procedure involved some uncertainty because of the upward displacement of the model with respect to the platform, relatively good agreement was found between the results obtained by the two methods.

The results for the train model with the trucks and wheels removed, table 4, show differences of about 5 percent, the ground-plane method giving the higher value. When the wheels and trucks were in place, the drag of the model was considerably greater, and the two methods gave substantially the same result. The difference between the results obtained by the two methods when the trucks and wheels were removed is presumably associated with the presence, in close proximity, of large, smooth surfaces in the ground-plane method, the drag being largely skin friction. Since neither method corresponds to the actual case in which the train moves relative to the ground and the air is at rest relative to the ground, it is not known which value is the more nearly applicable to a moving train.

TABLE 4.—$\frac{D}{V^2}$ *for train models* [a]

Figure 1 (B)

Body clearance	Ground-plane method, faired leading edge	Image method	Remarks
Inch			
¼	0.000198±0.2%	0.000189±0.2%	Without trucks and wheels (A=0.091 sq ft).
1¼	0.000218±0.2%	0.000209±0.1%	Without trucks and wheels (A=0.091 sq ft).
1¾ [b]	0.000367±0.2%	0.000374±0.1%	With trucks and wheels (A=0.111 sq ft).

[a] D refers to net drag of 1 model.

[b] Corresponds to wheel clearance of 3/16 inch.

3. DISCUSSION

The foregoing results indicate a possible source of discrepancy between the image and ground-plane methods. The speed of the air which acts on an object close to the ground plane is not the same as the speed of the air acting on the object several feet above it because of the presence of the boundary layer. In the experiments the beveled leading edge gave rise to a rapid decrease in velocity pressure beginning about 4 inches above the surface of the platform, corresponding to a comparatively thick boundary layer. For this reason agreement between the results of the two methods would not be expected. On the other hand concordant results were obtained when the faired leading edge was used, the velocity pressure in this case remaining practically uniform to within about 1 inch of the ground plane.

The results of the velocity traverse indicate the relative thicknesses of the boundary layers in the two instances. A model tested on the platform 2 feet aft of the beveled leading edge would obviously be subjected to a lower average velocity than when tested 2 feet aft of the faired leading edge, the reference speed being the same in the two cases. The result would be to cause lower drag measurements in the case of the beveled leading edge. The results of the drag tests on the streamline automobile model, table 2, indicate the presence of an effect of this nature. Hence, in using the ground-plane method for determining the drag of streamline models it appears desirable to use a platform with a faired leading edge and to conduct the experiments sufficiently far downstream from the leading edge to obviate its effect on the drag of the model. The present measurements indicate that a distance of at least two model lengths is desirable.

III. CONCLUSION

In testing vehicle models in the wind tunnel some method must be used to represent the effect of the ground on the full-scale vehicle. A comparison of experimental results by the ground-plane and image methods indicates that good agreement may be expected if the leading edge of the ground plane is faired and the tests are conducted at least two model lengths behind the leading edge. The ground plane should extend completely across the air stream in order to maintain a uniform velocity distribution across the test section.

WASHINGTON, August 24, 1934.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP749

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AIR FORCES AND YAWING MOMENTS FOR THREE AUTOMOBILE MODELS

By Roy H. Heald

ABSTRACT

The lift, drag, cross-wind force, and yawing moment for three models representing automobiles having substantially different body shapes were measured in the wind tunnel. Measurements were made for relative wind angles, in the horizontal plane, between 0 and 180 degrees. The results of the model investigation, extrapolated to full scale, indicate the presence of rather large lift, lateral force, and yawing moment under certain conditions of car speed and natural wind speed.

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I. INTRODUCTION

The early measurements of the air forces on automobile models in wind tunnels were confined, largely, to the measurement of the air resistance at the zero degree angle of yaw. Generally speaking the purposes of such tests were to find shapes of low air resistance and to furnish a basis for estimating the magnitude of the full-scale resistance due to motion in still air. Recently attention has been directed also to the effects of side winds.[1, 2]

The system of aerodynamic forces which acts on an automobile moving relative to the air is analogous to that which acts on an aircraft in flight. These forces arise as the result of local differences in air pressure, the net effect of the local pressures being to give rise to a tendency to motion in a certain direction. The magnitude and direction of this tendency can be represented by a single resultant force. In rectilinear motion through still air, or in horizontal head or tail winds, the resultant of the air forces acts in the vertical plane of symmetry of the vehicle. In this case the resultant may be defined in terms of lift, drag, and pitching moment about some fixed point in the vehicle such as the center of gravity. The introduction

[1] BS J. Research **11**, 285 (1933) RP591.
[2] Auto. Indus. **71**, 172 (1934).

of a quartering horizontal wind gives rise to a relative wind which acts at an angle to the direction of motion, somewhat less than the angle of the natural wind.

As a consequence of the new set of conditions, there is no plane of symmetry and 3 forces and 3 moments are necessary to define the resultant completely. Choosing axes with origin at the center of gravity, the three forces are the longitudinal force, in the direction of motion of the car (positive when opposing the motion), the lateral force, in a horizontal direction at right angles to the longitudinal force (positive when to the left looking forward), and the lift (positive when directed upward). The three moments are the pitching mo-

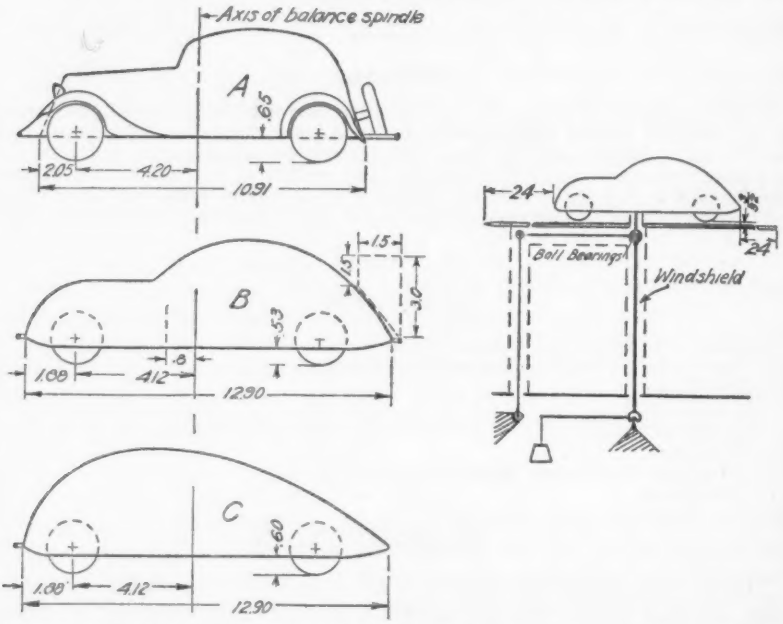

FIGURE 1.—*Models used in making force and yawing moment measurements.*

The scale was about 1:15. The dimensions are given in inches. The sketch at the right indicates the method used in measuring the drag and cross-wind forces.

ment about the lateral axis, the rolling moment about the longitudinal axis, and the yawing moment about the vertical axis.

Because of the interest in the limited data on the longitudinal and lateral forces reported in the Bureau's Research Paper 591, and because it appeared desirable to obtain further information on the models exhibited at the Century of Progress Exposition, a more extensive series of measurements has been made on these models, including the measurement of lift and yawing moment as well as longitudinal and lateral forces. The present paper describes the experiments.

II. DESCRIPTION OF MODELS AND METHOD OF TESTING

Outline drawings showing the principal dimensions of the models used for the experiments are given in figure 1. The models were those used in the tests previously reported, [3] models A, B, and C

[3] BS J. Research 11, 285(1933) RP591.

corresponding respectively to models 4, 5, and 6 of the earlier tests. In the earlier tests, measurements were made only for the "head-on" wind condition, a model being suspended by four wires in the wind tunnel with its wheels just clearing the surface of the ground plane. The displacements due to the wind were measured for a number of speeds and the drag computed from the displacement, the swinging radius, and the weight. A correction was applied for the resistance of the wires.

The method of measuring the forces on the models in the present investigation is indicated in figure 1. The measurements were made using an NPL type balance, care being taken to shield all exposed parts of the balance and fittings in order to reduce the spindle correction to a minimum. A parallelogram linkage attached to the balance in the 54-inch wind tunnel was used for making the drag and cross-wind force measurements. Such an arrangement obviated the necessity of determining the center of pressure of the model and spindle combination but did not permit simultaneous observations of drag and cross-wind force. The lift and yawing-moment measurements were made using the regular equipment of the NPL balance, the lift being determined by means of the vertical lift attachment of the balance and the yawing moment by means of the standard torque balance.[4]

Previous tests [5] having shown a marked effect of the shape of the leading edge of the ground plane on the resistance of a streamline model, an investigation was made of the velocity distribution over a platform extending entirely across the air stream, which was used to represent the ground. The faired section of the upstream edge of the platform is indicated in figure 1. The mean air speed at the test section, 2 feet downstream from the leading edge of the ground plane, was determined from a traverse of an area 6 inches square in the plane of the balance spindle, observations being made at some 30 stations. The air speed was found to be substantially uniform down to within one-half inch of the ground plane. It would be expected therefore that the effects on the model arising as a result of the interaction of the boundary layer of the platform with the air flow around the model would be confined to the region of the wheels since the lower surface of each model, as mounted in the test position, was some half inch above the ground plane when the wheels were just clear.

III. RESULTS

1. FORCE TESTS

The experimental arrangement simulated the conditions encountered when an automobile is driven in a quartering horizontal wind, the direction of the air stream in the wind tunnel representing the direction of the relative wind resulting from the natural horizontal wind and the motion of the car. While the natural wind may have a vertical component, the magnitude of that component is probably very small within the height of an automobile above the ground. It was convenient to measure the components of the resultant force along and perpendicular to the direction of the relative wind, i.e., the drag and cross-wind force, and to compute from them the compo-

[4] Tech. Rep. 72 Nat. Adv. Comm. Aeron.
[5] J. Research NBS **13**, 863 (1934) RP748.

nents along and perpendicular to the normal direction of motion of the car, i.e., the longitudinal and lateral forces.

Measurements were made at intervals of 10° from 0 to 180°, 0° corresponding to a head-on wind, 180° to a tail wind. The net observed force, F, in pounds, was divided by the product of A, the maximum frontal area, projected normal to the longitudinal axis

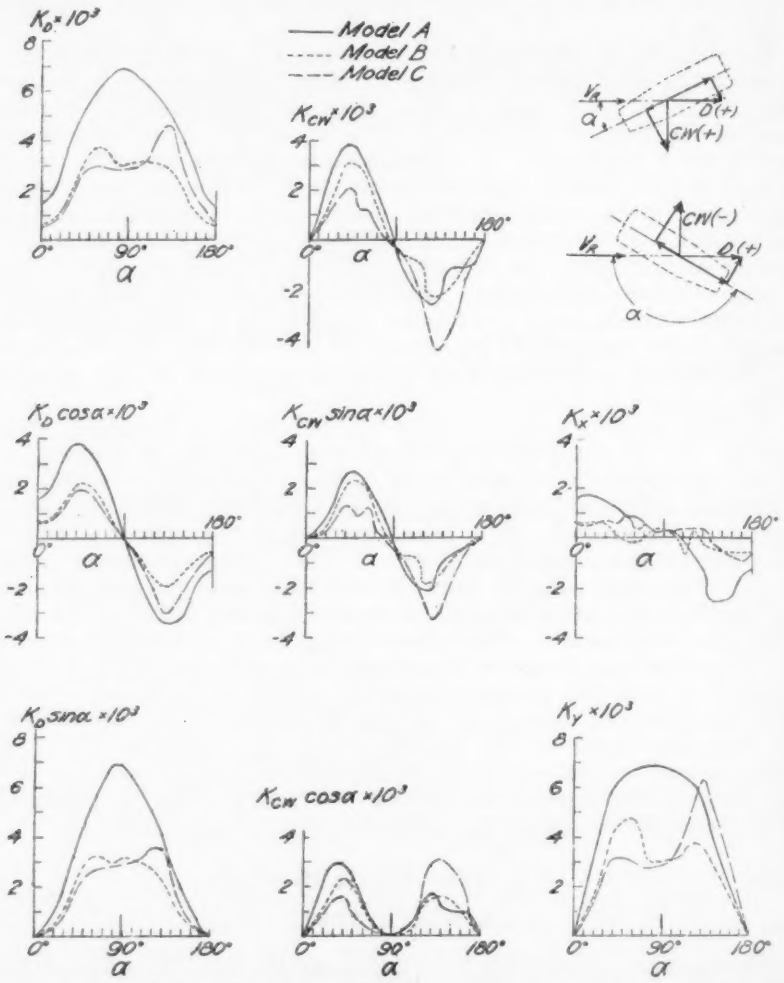

FIGURE 2.—*Resolution of the drag and cross-wind force coefficients to give longitudinal- and lateral-force coefficients.*

of the model, in square feet, and the square of the relative air speed, V_R, in miles per hour, to obtain a coefficient, K.

Thus $K=\frac{F}{AV_R^2}$. Subscripts are used to denote the several components, D for drag, CW for cross-wind force, X for longitudinal force, Y for lateral force, L for lift. The relations between drag and cross-wind force coefficients, and longitudinal and lateral force coefficients are as follows:

$$K_x = K_D \cos\alpha - K_{CW} \sin\alpha$$

$$K_y = K_D \sin\alpha + K_{CW} \cos\alpha$$

where α is the angle of yaw, corresponding to the angle of relative wind in the full-scale case.

The longitudinal and lateral force coefficients are plotted in figure 2, and as a matter of interest, the contributions of the drag and cross-wind force to the longitudinal and lateral force are also plotted.

The positive directions of the drag and cross-wind force are indicated in figure 2. The longitudinal force is considered positive when opposite to the direction of motion of the car; when positive, the longitudinal force retards the car; when negative, it aids the motion of the car. The lateral force is considered positive when directed to the left, looking forward. The lift coefficients, plotted in figure 3, are considered positive when the lift is directed upward.

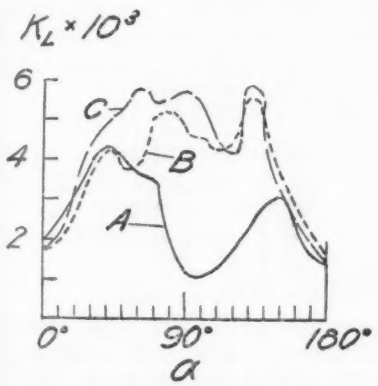

FIGURE 3.—*Lift coefficients.*

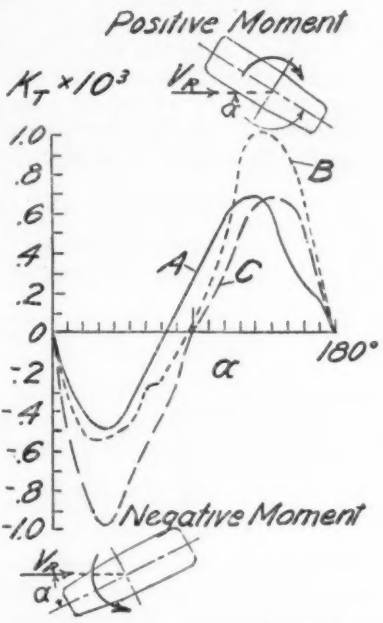

FIGURE 4.—*Yawing moment coefficients.*

2. MOMENT TESTS

The axis about which most of the yawing moments were measured was half-way between the front and rear axles. (Axis of balance spindle in figure 1.) The yawing moment, M, in pounds-feet, was divided by the product of AV_R^2, and l, the overall length of the model, in feet, to give the yawing moment coefficient K_T, plotted in figure 4. The direction of yawing moment is considered positive when the moment tends to reduce the angle between the longitudinal axis of the body and the direction of the relative wind.

Generally speaking, streamline bodies moving in still air, without interference from surrounding objects, are directionally unstable in an aerodynamic sense, i. e., when yawed with respect to the direction of motion the tendency of the resulting moment is to increase the yaw. The degree of instability is partly dependent on the magnitude and shape of the exposed areas ahead of and behind the center of

gravity and it might be expected that the streamline models in the presence of the ground plane would exhibit somewhat the same characteristics. The moment curves in figure 4 show that all three models are aerodynamically unstable when the vertical plane containing the center of gravity is assumed to be half-way between the front and rear axles, an assumption believed to be fairly representative of actual cases. Obviously there are two methods of improving stability: (1) by moving the center of gravity forward, and (2) by adding effective area behind the center of gravity as, for example, by the use of fins. A few experiments dealing with the question of stability were made and for these, model *B*, figure 1, was selected. It will be noted from table 1 that the model was brought into approximately neutral condition, for the case of relative wind from the forward quarter, by using three fins of equal areas, uniformly spaced laterally. The total area of the fins represented about 90 percent of the maximum projected frontal area of the model.

TABLE 1.—*Stability measurements (model* B, *fig. 1)*

Values of $K_T \times 10^3$ for various angles of relative wind (α).

α	Without fins	With 3 fins	Without fins; center of moments moved ahead 0.8 inch	With 3 fins; center of moments moved ahead 0.8 inch
Degrees				
0	0.00	0.00	0.00	0.00
10	−.32	+.07	−.28	+.09
20	−.51	−.04	−.43	+.15
30	−.54	+.04	−.41	+.33
50	−.43	−.05	−.17	+.33
70	−.27	+.25	−.13	+.58

Moving the assumed position of the center of gravity (axis of moments) ahead a distance equivalent to about 1 foot, full scale, substantially reduced the unstable moment within the range of angles investigated. The model was made completely stable, as regards wind from the forward quarter, by a combination arrangement which consisted in moving the assumed position of the center of gravity ahead 0.8 inch (about 1 foot, full scale) and using the three fins. It may be noted in this connection, however, that whatever is gained by the use of fins, as regards stability with respect to wind from the forward quarter probably represents a corresponding loss with respect to winds from the rear quarter.

IV. DISCUSSION

A noteworthy result of the tests is to indicate the behavior of the longitudinal force coefficient in the case of the streamlined models and, in particular, model B. The coefficient changes sign twice in the first quadrant and three times in the second quadrant. Although the longitudinal force coefficient was obtained, by computation, as the difference of two larger quantities, as indicated in figure 2, the presence of experimental errors amounting to several percent in the original observations would be required to account for this behavior. It appears more probable that the changes were caused by the alternate preponderance of the drag and cross-wind components as the angle of yaw was increased.

Another outstanding characteristic common to all three models is the occurrence of comparatively large lateral forces. In the first quadrant both streamline models were found to have lateral forces of the order of one-half the lateral force on the model of the conventional car. In the latter part of the second quadrant, however, the lateral force on streamline model C exceeded the lateral force on the model of the conventional car.

Between 0 and 40° yaw the lift of all three models was of about the same order of magnitude. In the neighborhood of the broadside position, however, the lifts of both faired models were found to be considerably greater than the lift of the model of the conventional car. A relationship of this kind between the lift forces might be expected as a result of the somewhat greater curvature in lateral section of the streamline models.

The yawing moment curves of the three models exhibit the same general characteristics. All were found to be unstable for the position originally assumed for the center of gravity. The torque measurements made with several different fin combinations on model B indicate that a total fin area of approximately 90 percent of the maximum projected frontal area would be required to bring the full scale car to a stable condition with respect to relative winds from the forward quarter.

V. ESTIMATES OF FULL-SCALE VALUES

The equations for determining the magnitude, V_R, and the direction, angle α, of the relative wind, having given the magnitude, V_w and the direction, angle β, of the natural wind and the velocity of the vehicle, V_A, are:

$$V_R = \sqrt{V_A^2 + V_w^2 + 2V_A V_w \cos \beta}$$

$$\alpha = \sin^{-1} \frac{V_w \sin \beta}{V_R}$$

The magnitudes of the forces and torques are dependent on the velocity and angle of the relative wind. These are dependent, in turn, on the velocity of the vehicle, (V_A), the velocity, (V_w), and the direction, angle β, of the natural wind which is here considered to act in the horizontal plane. Thus there are an indefinite number of combinations of car velocity, natural wind velocity, and natural wind direction that can occur, each combination corresponding to a relative wind whose magnitude and direction can be computed.[6] Certain combinations give rise to a relative wind at 90° to the direction of motion and in some cases the angle of the relative wind may be greater than 90° to the direction of motion, as for example, when the natural wind blows nearly from the rear at a speed greater than that of the car.

In order to illustrate the orders of magnitude of the full-scale forces the values given in table 2 have been computed for full-scale replicas of models A, B, and C, figure 1, assuming a driving speed of 50 miles per hour. The coefficients shown in figures 2, 3, and 4 were used in the computation assuming a frontal area, previously defined, of 25 square feet and a body length of 15 feet. The forces given in

[6] J. Soc. Auto. Engrs., **33**, 18, (November 1933).

the table have been rounded to the nearest 10 pounds, the moments to the nearest 10 pounds-feet. The effects of scale and of projections, such as the undercarriage, present on the full-scale car but not represented on the model, cannot be predicted accurately. The assumed driving speed is believed to be representative. Driving in continuous winds of 10 miles per hour is common and gusts of 30 to 40 miles per hour may be encountered.

TABLE 2.—*Forces and yawing moment for full-scale replicas of the models, scale effect neglected*

V_A=car speed=50 mph
V_w=wind speed=10 and 30 mph
β=angle of natural wind=0, 45, 90, 135, and 180 degrees.
α=angle of relative wind.

X=longitudinal force (lb).
Y=lateral force (lb).
L=lift (lb).
T=yawing moment (lb feet).

V_w=10 mph

β	α	Model A				Model B				Model C			
		X	Y	L	T	X	Y	L	T	X	Y	I	T
°	°												
0	0.0	140	0	180	0	50	0	150	0	50	0	150	0
45	7.1	140	83	190	160	50	40	160	240	40	40	170	310
90	11.3	110	104	170	200	40	50	140	280	30	40	140	380
135	9.4	80	66	120	120	30	30	90	180	20	30	100	220
180	.0	60	0	80	0	20	0	70	0	20	0	70	0

V_w=30 mph

0	0.0	240	0	320	0	100	0	270	0	100	0	270	0
45	16.6	230	350	400	550	90	170	340	770	80	140	370	1120
90	31.0	130	410	340	470	50	250	310	570	60	200	370	1000
135	36.3	50	190	140	180	10	120	130	210	20	90	150	370
180	.0	20	0	20	0	10	0	20	0	6	0	20	0

VI. CONCLUSION

Broadly speaking the aerodynamic problem placed before the designer is to find the vehicle body shape requiring the minimum amount of power to overcome the air forces and having satisfactory stability. From this viewpoint it is necessary to consider the action of all forces which arise as a result of relative motion between the full-scale automobile and the air.

Bearing in mind the limitations imposed on the model method, the results of the present experiments indicate that substantial reduction in the longitudinal and lateral forces, throughout the 0 to 180° range of relative wind angles, is to be expected from the use of streamline body forms. However, the lift forces and yawing moments may be somewhat greater for certain ranges of angles of relative wind in the case of streamline body forms. The results of the extrapolation from the model measurements to full-scale point to the possibility of rather large lateral forces and yawing moments for all three types of bodies at high car and wind speeds.

WASHINGTON, August 24, 1934.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP750

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PERMEABILITY OF SYNTHETIC FILM-FORMING MATERIALS TO HYDROGEN

By Theron P. Sager

ABSTRACT

The permeabilities to hydrogen of a number of synthetic film-forming materials spread on closely woven cotton fabric have been determined. Of the films studied, those in which the molecule is rich in hydroxyl groups, regenerated cellulose sheet and polyvinyl alcohol being examples, show very low permeabilities. Cellulose esters and polyvinyl acetate on the contrary give high values. A rough parallelism may be said to exist between the permeabilities of continuous films and the solubility of hydrogen in corresponding types of compounds of simple structure. A comparison of the permeabilities explains the extensive use of materials having hydrophilic-colloidal properties as coating materials for gas-cell fabrics. That satisfactory coating materials may not be limited to highly hygroscopic substances is indicated by the permeabilities obtained with several materials less affected by moisture.

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I. INTRODUCTION

The nature of the process by which gas passes through rubber has been the subject of numerous studies. To Graham [1] belongs the credit of first noting that the relative rates of diffusion of different gases through rubber bear no relation to their densities or viscosities. He concluded that in the absence of microscopic openings permeation takes place entirely by a process of solution in the rubber on one side and subsequent evaporation from the other side. Concerning the permeability of other continuous films very little information is available in the literature. Kanata [2] investigated gelatin and celluloid as well as rubber and showed that diffusion through these substances is likewise the result of solvent action. Northrup [3] also found that collodion membranes behave like rubber toward gases.

If we assume that gases pass through all continuous films by a process of solution, we should be able to predict the rate of diffusion through a particular type of film-forming material, reasoning from

[1] Phil. Mag. **32**, 401 (1866).
[2] Bull. Chem. Soc. Japan **3**, 183 (1928).
[3] J. Gen. Physiol. **12**, 435 (1929).

the solubility of hydrogen in analogous types of compounds of simple structure.

There are many synthetic film-forming materials that are particularly suited to the study of this relation of composition to permeability because their chemical composition and molecular structure have already been extensively studied. In addition to their value for the present study, many of them are of practical interest in connection with the investigation of gas-cell fabrics conducted in collaboration with the Bureau of Aeronautics, Navy Department. Few structural materials have such rigid and varied requirements as gas-cell fabric. Besides being impermeable to lifting gases, a gas cell, which requires several thousand yards of fabric, must be light in weight, possess a high strength-weight factor, and be capable of withstanding use and handling under varied atmospheric temperatures and humidities. It is of interest to note that two of the earliest balloon fabrics are prototypes of those used today. In 1783 Charles and the Robert brothers built a balloon of taffeta covered with rubber. During the same year, Baron de Beaumanoir constructed a small balloon lined with goldbeater's skin. In the early nineties, the first dirigibles of the Santos-Dumont type employed varnished fabrics that proved unsuitable because of their tendency to crack, and were soon replaced with heavy rubberized fabric. With the development of the Zeppelin type of airship, the need arose for a lighter and less permeable material. In 1908 the Zeppelin Co. installed experimental gas cells made with goldbeater's skins, and in 1914 they equipped an entire ship with this type of cells. The objection to cells made of goldbeater's skin is chiefly one of expense, which has become almost prohibitive by the increase in size of the present-day ships. The trend of modern development has been largely directed toward the improvement of rubberized fabrics and the use of gelatin and regenerated cellulose in conjunction with rubber.

The general problem of gas-cell fabrics in relation to airship problems is discussed in detail by Fulton.[4] The present paper is confined to the discussion of permeability to hydrogen. The application of particular materials to gas-cell fabrication is complicated by problems of plasticizing, seaming, cost, and method of manufacture. In view of these factors, the relative utility of all the materials mentioned herein for actual gas-cell construction is not necessarily indicated by their degree of permeability.

II. EXPERIMENTAL PROCEDURE

1. PREPARATION OF SAMPLES

With the exception of one commercial sheet material, all the samples were prepared by coating cotton fabric with the film-forming material. This method of preparing the film has the advantage of convenience, particularly with materials which need the structural reinforcement of the fabric, and the advantage of direct information regarding the permeability of the film supported by fabric in the manner customary in the construction of gas cells. The presence of fabric influences the permeation of gases through rubber. Edwards and Pickering [5] found that spreading rubber on fabric reduced its

[4] J. Am. Soc. Naval Eng. **41**, 47 (1929).
[5] BS Sci. Pap. **16**, 327-362 (1920) S387.

apparent permeability to gases. It has been found that the construction of the supporting fabric has an effect. This is indicated by the values given in table 1, for rubberized fabrics in which the supporting fabrics had different weights and thread counts. The results indicate that permeability decreases with increase in thread count. In the present work the same fabric was used throughout in order to make the effect of the fabric a constant in the comparison of the permeability ratings for the different coatings.

TABLE 1.—*Variation in permeability of rubberized fabrics of different thread count*

Weight of cloth	Threads per inch		Weight of rubber	Permeability at 1 atmosphere
	Warp	Filling		
oz/yd²			oz/yd²	l/m²/24 hr
1.5	132	134	0.9	38.5
1.6	198	172	.9	24.0
2.2	125	132	.9	44.0
2.0	133	124	.9	47.8
1.6	134	133	.85	36.3

Two methods of preparing the coated fabrics were employed. The simplest method was to tack the raw fabric on a 12 by 12-inch frame and apply the coating material, dissolved in a suitable solvent, by brushing on several coats. The solvent was allowed to evaporate thoroughly between coatings. This method yields an area of fabric sufficient for the permeability determination. A more laborious and time-consuming method is to apply the coating with a small laboratory spreader. In this the fabric is held under tension and the solution of the coating material is evenly applied with a movable doctor blade. Samples 20 by 50 inches were prepared in this way. By employing the same solvents and applying the same number of coats, approximately the same permeability values are obtained on samples prepared by the two methods.

2. MATERIALS

The raw fabric was what is designated as HH balloon cloth and is the fabric largely employed in gas-cell construction. The specifications of this fabric are as follows:

Maximum weight per sq yd, oz	2.05
Maximum width, inches	42.5
Minimum width, inches	41.5
Minimum tensile strength, lb/in.:	
Warp	38
Filling	38
Ply of yarns:	
Warp	1
Filling	1

The types of film-forming materials investigated are given in figure 1. Where possible, their most commonly accepted structures are included.

The regenerated cellulose was sheet cellophane not moistureproofed. The material was approximately 0.001 inch thick. It contained about 16 percent of glycerol as a softener. The polyvinyl alcohol was prepared from polyvinyl acetate of high viscosity by hydrolysis with an alcoholic solution of potassium hydroxide, according to the method described by Staudinger, Frey, and Stark.[6] The polyvinyl alcohol

[6] Ber. 60, 1789 (1927).

was washed repeatedly with alcohol and finally dialyzed through washed cellophane. Polyvinyl alcohol is soluble in water and insoluble in other solvents. The cellulose acetate was acetone soluble. The cellulose nitrate was one-half second cotton of lacquer grade. The cellulose aceto-stearate was furnished us as an experimental material.

The polyvinyl acetal was prepared by adding freshly distilled acetaldehyde to an aqueous solution of polyvinyl alcohol containing

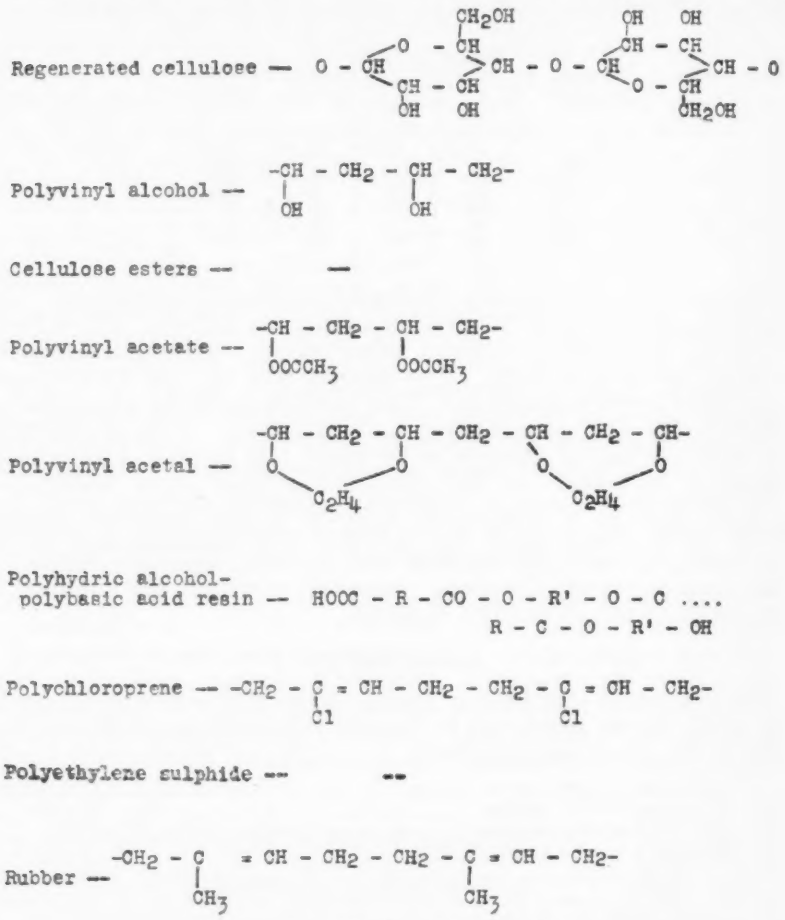

FIGURE 1.—*Film-forming materials.*

a small amount of hydrochloric acid as a catalyst. The solution was maintained at 65° C and thoroughly stirred. The acetal resin precipitated from the solution in the form of a rubbery mass. This was washed to remove adhering acid by comminuting with water, dissolved in ethyl alcohol, and precipitated from the alcohol solution by diluting with water. This was repeated until the material gave no test for acid.

Of the polyhydric alcohol-polybasic acid resins the phthalates, succinates and sebacates were prepared according to methods described

by Carothers and Arvin,[7] and by Kienle and Hovey.[8] The citrates were prepared according to the method described by Sager [9] in the preparation of tetraethylene glycol citrate. No attempt was made to obtain resins of exceptional purity. In the preparation of products in which both reactants contained two reactive groups, i.e., glycols and dicarboxylic acids, the esterification was carried as nearly to completion as possible. When the tri-reactive materials, glycerol and citric acid, were employed, the esterification was halted by quenching in air just prior to the point of gelation. The fabric-supported films made from these resins represent the resins in this condition without any further heat treatment. The gas-cell fabric coated with Duprene (polychloroprene) represented experimental factory production. The ether-soluble rubber has been described by Smith, Saylor, and Wing.[10] A small amount of *N*-phenyl-β-naphthylamine was added as an anti-oxidant. The curing was done with sulphur chloride. The smoked sheet rubber was milled for 10 minutes and was likewise cured with sulphur chloride. The polyethylene sulphide was a rubber substitute known as Thiokol A. This was applied to the fabric by a calendering operation.

3. DETERMINATION OF PERMEABILITY

The permeabilities were all determined by a method developed at the National Bureau of Standards and previously described.[11] Briefly the method consists in measuring by means of a gas interferometer the difference in refractivity of gas as contained in chambers on the two sides of the fabric. The fabric is held at a temperature of 25° C with air at atmospheric pressure on one side of the fabric and hydrogen at an excess pressure of 30 mm of water on the other side.

The permeabilities to hydrogen are given in table 2 together with the weight per unit area of each film. This weight is obtained by subtracting the weight of the uncoated fabric from that of the coated fabric. All weighings were made at approximately 70° F and 65 percent relative humidity. The application of the same weight of coating to each piece of fabric was not feasible. For comparing the relative permeabilities the product of the permeability and weight has been included. For comparing rubberized fabrics this product is useful since for this material the value has been found, within certain weight ranges, to be practically a constant. The propriety of using this product for comparing a variety of materials may be questioned since the validity of regarding this product as a constant for all materials has not been established.

The permeabilities are expressed as liters per square meter per 24 hours. For conversion to cubic feet per square yard per 24 hours this value should be multiplied by 0.0295.

[7] J. Am. Chem. Soc. **51,** 2568 (1929).
[8] (J. Am. Chem. Soc. **51,** 509); **52,** 3636 (1930).
[9] Ind. Eng. Chem., Anal. ed. **4,** 388 (1932).
[10] BS J. Research **10,** 479 (1933) RP544.
[11] BS Techn. Pap. **11,** (1918) T113. BS Sci. Pap. **16,** 327-362 (1920) S387.

TABLE 2.—*Permeabilities of film-forming materials*

Material	Solvent	Permeability at 1 atm	Weight		Permeability × weight
		l/m²/24 hr	oz/yd²	g/m²	l/m²/24 hr × g/m²
Regenerated cellulose sheet (cellophane)		0.1	1.5	51	5
Polyvinyl alcohol	Water	.1	2.0	68	7
Do	do	.2	1.9	64	13
Polyvinyl acetal	Ethanol	.7	2.9	98	69
Polyhydric alcohol-polybasic acid resins:		.4	2.6	88	35
Ethylene glycol citrate	do	.1	3.2	109	11
Diethylene glycol citrate	do	.1	3.5	119	12
Glycerol phthalate	Ethyl acetate, 10 percent; acetone, 90 percent.	.2	3.6	122	24
Ethylene glycol phthalate		.3	3.7	125	38
Diethylene glycol phthalate		.5	3.1	105	53
Glycerol succinate		1.0	2.4	81	81
Diethylene glycol succinate		.9	3.2	109	98
Glycerol sebacate		1.1	3.3	112	132
Diethylene glycol sebacate		1.6	3.0	102	163
Polyvinyl and cellulose esters:					
Polyvinyl acetate (high viscosity)	Ethanol	4.7	2.7	92	432
Do	do	3.1	2.9	98	304
Polyvinyl acetate (low viscosity)	do	10	2.8	95	950
Do	do	13	2.9	98	1,270
Cellulose nitrate	Mixture 2	7.4	3.6	122	903
Do	do	9.5	3.3	112	1,060
Cellulose acetate	Mixture 1	15	2.3	78	1,170
Do	do	21	1.8	61	1,280
Cellulose aceto-stearate	Benzol	17	2.7	92	1,560
Rubber substitutes:					
Polyethylene sulphide (Thiokol A)		.2	9.5	322	64
Do		.5	5.2	176	88
Polychloroprene (Duprene)		5.9	3.6	122	720
Ether-soluble rubber	Toluol	9.3	2.8	95	883
Smoked sheet rubber		19	2.0	67	1,273
Do		22	1.7	57	1,307

Solvent mixture 1.—Ethylene dichloride 60 percent, ethyl alcohol 10 percent, methyl cellosolve 10 percent, cellosolve acetate 5 percent, ethyl acetate 15 percent.
Solvent mixture 2.—Toluol 20 percent, ethyl alcohol 60 percent, ethyl acetate 10 percent, cellosolve 10 percent.

III. DISCUSSION OF RESULTS

A comparison of the permeability-weight products given in table 2 indicates that the chemical composition of a continuous film is the controlling factor in the process of permeation of hydrogen. In this list of materials are those which have consistently indicated a fibrous or pseudocrystalline structure and those which are characterized by an amorphous structure. The degree of polymerization likewise varies over an enormous range. No clearly defined correlation appears to exist with regard to these properties.

In the case of some of the materials a fairly close parallelism may be drawn between their permeability and the solubility of hydrogen in compounds of the same type but of simple structure. Very low permeabilities are encountered with materials rich in hydroxyl groups such as regenerated cellulose sheet and polyvinyl alcohol. Hydrogen is but slightly soluble in water and glycerol, analogous compounds of simple structure. The behavior of the polyvinyl acetal and the polyhydric alcohol-polybasic acid resins is believed to be attributable to the presence of residual hydroxyl groups in the molecule. The method of preparation of the polyvinyl acetal yields a product which by its behavior toward solvents and its hygroscopic nature indicates incomplete formation of acetal groups in the molecule. It is believed that the presence of the residual hydroxyl groups is more of a determining factor contributing to the low permeability than any inherent char-

acteristic of the acetal type of compound. The same reasoning may be applied to the polyhydric alcohol-polybasic acid resins. The formation of these resins has been shown to yield polymeric esters which take the form of long chains with the dihydric alcohol-dibasic acid reactants and branched chains in the case of the tri-reactive substances such as glycerol and citric acid. In either case the end groups are represented as COOH and OH. These resins are all hygroscopic, this property being less pronounced in the case of the sebacates, which have the highest permeabilities in this list of resins.

The behavior of the polyvinyl and cellulose esters indicates the marked effect upon the permeability with the introduction of ester groups in these molecules. A parallelism may be cited with the relatively high solubility of hydrogen in simple esters. The behavior of rubber likewise has its analogy in the simple hydrocarbons.

The comparatively low permeability obtained with polyethylene sulphide (Thiokol A) is of interest inasmuch as this represents a compound of a different type. A parallelism may be suggested between this material and carbon disulphide, in which the solubility of hydrogen is low in comparison with esters and hydrocarbons. It is unfortunate that the calendering operation did not permit the application of a weight of coating comparable with the other materials examined but it is of interest to note that of the two samples examined the permeability-weight products are of approximately the same order of magnitude.

The claim of lower permeability for polychloroprene (Duprene) than natural rubber [12] is substantiated.

The lower permeability obtained with ether-soluble rubber is of possible significance in indicating the behavior of the more plastic form of the rubber hydrocarbon. In the absence of similar data on the gel-rubber constituent, no definite conclusions can be drawn.

From a practical point of view the relative permeabilities illustrate why, in the construction of gas-cell fabrics, materials having hydrophilic colloidal properties have been used so extensively as coatings on fabric for the retention of lifting gases. For numerous reasons, particularly the variation in weight with changes in atmospheric humidity, the use of highly hygroscopic materials is admittedly undesirable. The permeabilities of several materials which are less affected by the presence of moisture indicates that these or materials of similar nature possibly may be employed.

The work reported in this paper was done as a part of an investigation conducted under Bureau of Aeronautics Project NBS no. 5319 on Gas-Cell Fabrics. The interest of the Bureau of Aeronautics, Navy Department, in this work and permission to publish these results is hereby acknowledged. Acknowledgment is also made to E. C. Creitz, who determined the permeabilities.

WASHINGTON, September 27, 1934.

[12] Ind. Eng. Chem. **26**, 36 (1934).

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PHOTOELASTIC PROPERTIES OF SOFT, VULCANIZED RUBBER

By Wilfred E. Thibodeau and Archibald T. McPherson

ABSTRACT

A study of double-refraction under tensile stress was made on transparent, vulcanized rubber at about 25° C by means of a Babinet compensator, using light of wave length, 5461 A. The relative retardation per unit thickness and the stress-optical coefficient were found to be related to the stress by equations of the form, $\Delta n = aT + bT^2 + cT^3$, and $C = a + bT + cT^2$, where Δn is the retardation coefficient, C the stress-optical coefficient, T the stress, and a, b, and c are constants for any given rubber compound. Formulas of the compounds investigated, in parts by weight, were: pale crepe rubber, 100; stearic acid, 1; and zinc oxide, 1, to which was added—(A) "captax" (mercaptobenzothiazole), 1, "tuads" (tetramethylthiuramdisulphide), 0.5, selenium, 0.5, and sulphur, 0.3; (B) "tuads", 0.3, and sulphur, 2.0; (C) "tuads", 0.3, and sulphur, 4.0; (D) "captax", 0.5, and sulphur 2.5; (E) "captax", 0.5, and sulphur, 4.0; (F) to (J), inclusive, sulphur, 3 to 7, respectively. Compounds (K), (L), and (M) were made from rubber hydrocarbon with 4, 6, and 8 percent of sulphur, respectively. The parameters, a, b, and c, were functions of the type of compound. A term in c was needed, if at all, only at stresses above 65 bars. For compounds A to E, inclusive, values of $a \times 10^4$ were 2.059, 2.092, 2.233, 2.155, 2.242, respectively; values of $b \times 10^4$ were 0, 0, −0.00354, 0, −0.00146, respectively. For compounds F to M, inclusive, a and b were functions of the percentage of combined sulphur, and the retardation coefficient was given by the equation,

$$\Delta n \times 10^4 = (1.960 + 0.0250\ S_c)\ T - (0.00540 + 0.00112\ S_c)\ T^2,$$

where S_c is the percentage of combined sulphur.

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I. INTRODUCTION

This paper describes an exploratory study of the photoelastic properties of transparent, soft, vulcanized rubber. The work was originally undertaken to obtain data on rubber samples that were used in an investigation of stresses in models by the photoelastic

[1] W. E. Thibodeau, unpublished work.

method,[1] and was extended to provide general information on the relation of the photoelastic properties to the composition of rubber.

Measurements of the photoelastic behavior of rubber have been made by several previous investigators whose work points to a functional relation between double-refraction and stress. Bjerken [2] made measurements on rubber of unspecified composition at stresses from 5 to 69 bars, which corresponded to elongations from 66 to 434 percent. Rossi [3] observed the behavior of three types of rubber compositions, (1) crude rubber, (2) the same, mixed with oil and wax, and (3) rubber vulcanized with 15 percent of sulphur and subsequently extracted with benzene. Rossi's measurements extended only to stresses of 5 to 7 bars, which corresponded to elongations of 50 to 100 percent. The measurements of the coefficient of relative retardation by both Bjerken and Rossi, when plotted as functions of stress, give smooth curves which are either linear or nearly so. Van Geel and Eymers, [4] however, working with sheets of rubber made by the evaporation of latex, obtained a discontinuous relation between relative retardation and stress. Other investigators have studied the double-refraction of rubber in relation to the structure. This latter work is summarized in a recent paper by Rowland.[5]

The contribution of the present investigation lies in the fact that it presents measurements made over relatively wide ranges of stress and composition, and indicates that for any given rubber compound the relation between relative retardation per unit thickness and stress can be expressed by a simple equation. For certain compounds made with organic accelerators the relation may be simplified to a linear one, while for rubber-sulphur compounds the relation is a function of the combined sulphur content.

The present investigation leaves untouched a number of factors which may have important bearing on the photoelastic behavior of rubber. The measurements were all made at approximately the same temperature, that of the room, and with light of one wave length, the green line of mercury. The results obtained represent the behavior of rubber samples being stressed for the first time, and under conditions which produced no appreciable optical creep.

The definitions, symbols, conventions, and literature on photoelasticity up to 1931 are to be found in a recent comprehensive text on the subject by E. G. Coker and L. N. G. Filon, entitled "A Treatise on Photoelasticity", Cambridge University Press (1931).

II. PREPARATION OF SPECIMENS

The specimens for photoelastic measurement were made from three types of rubber compounds. Compounds of the simplest type were prepared from rubber hydrocarbon and sulphur, and were vulcanized so as to bring practically all of the sulphur into combination with the rubber. These are represented in table 1 by formulas K, L, and M, which were prepared in connection with an investigation on the electrical properties of rubber.[6] Compounds of another type were made from crude rubber and sulphur, together with small amounts of zinc oxide and stearic acid; the

[2] Ann. Phys. [3] **43,** 808 (1891).
[3] Il nuovo Cimento [5] **20,** 226; 268 (1910).
[4] Z. Phys. Chem. **3,** 240 (1929). English translation, Rubber Chem. Tech. **2,** 545 (1929).
[5] Ind. Eng. Chem. **22,** 1182 (1930); also, Rubber Chem. Tech. **4,** 83 (1931).
[6] BS J. Research **11,** 173–209 (1933); RP585.

two latter ingredients were introduced to render these compounds more nearly comparable to those of the third type in which accelerators were employed. The compounds made from crude rubber and sulphur are represented by formulas F to J, inclusive, and the compounds made with accelerators, by formulas A to E, inclusive. The accelerators employed were tetramethylthiuram disulphide and mercaptobenzothiazole, each with two different percentages of sulphur. One additional compound, A, was made using a combination of the two accelerators and a small percentage each of sulphur and selenium.

TABLE 1.—*Composition of samples*

Composition and treatment	Designation of rubber compounds												
	A	B	C	D	E	F	G	H	I	J	K	L	M
Constituents (parts by weight):													
Pale crepe rubber	100	100	100	100	100	100	100	100	100	100			
Rubber hydrocarbon											96	94	92
Zinc oxide (Kadox)	1	1	1	1	1	1	1	1	1	1			
Stearic acid	1	1	1	1	1	1	1	1	1	1			
Tetramethylthiuram disulphide	.5	.3	.3										
Mercaptobenzothiazole	1			.5	.5								
Sulphur	.3	2	4	2.5	4	3	4	5	6	7	4	6	8
Selenium	.5												
Conditions of vulcanization:													
Time (min)	45	30	40	60	60	300	300	300	300	300	(a)	(a)	(a)
Temperature (°C)	134	126	126	134	134	148	148	148	148	148			
Composition:													
Free sulphur, percent		.10	1.28	1.06	1.38	.04	.05	.09	.08	.08	(a)	(a)	(a)
Combined sulphur, percent		2.05	2.40	1.60	2.46	2.85	3.69	4.65	5.35	6.19			

[a] The preparation and composition of these samples are discussed in the paper cited in footnote 6.

The specimens were prepared in the familiar dumb-bell shape commonly used for tensile tests. The thinner specimens were cut with a die from molded sheets, but in the case of thicker specimens the preparation in this manner resulted in curved edges, so recourse was had to molding and vulcanizing such samples in the desired form. The molds consisted of frames provided with sheets of polished aluminum for covers. In making samples an excess of stock was placed in a mold which was pressed between the platens of a vulcanizing press at a temperature of about 100° C. All stock which overflowed was carefully removed and the mold then placed in a press at the requisite temperature for vulcanization. The specimens so prepared were uniform in thickness to a high degree. Fine reference lines were printed on the specimens at the time of vulcanization by ruling scratches on the aluminum sheets used for covering the mold, and filling these scratches with carbon black.

Specimens from 0.7 to 2.7 mm in thickness were employed. The constricted portion of the specimens was about 6.5 mm in width; the length between the reference marks was about 50 mm.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental observations which were made included the determination of the dimensions of the specimens, both in the unstressed and in the stressed condition, and the measurement of the relative retardation of the light vibrations respectively parallel and perpendicular to the direction of stress in the specimens.

The thickness and the width of samples in the unstressed state were measured by means of screw micrometer gages [7] which were thought to be reliable to about 0.0002 inch or 0.005 mm. Measurements of the length of rubber specimens, both before and during the application of stress, were made by means of an improvised cathetometer which operated with a precision of about 0.2 mm.

A few direct measurements of the thickness and the width of specimens under stress were made with the screw-micrometer gage, but in most instances these dimensions were computed from the original thickness and width, and the elongation, as will be discussed in a subsequent part of this paper.

The relative retardation, or the distance by which the extraordinary or slow wave lags behind the ordinary wave in passing through the sample under stress, was measured by means of the well-known Babinet compensator. The optical system consisted of a light source, a polarizing nicol furnishing light vibrating at 45 degrees to the direction of stress, the compensator, the sample under stress, an analyzing nicol at a position of extinction relative to the polarizer, together with a ground-glass screen and accessory projection components. The light source was a mercury arc from which light of wave length 5461 A was isolated by the use of an optical filter. The compensator had an aperture about 3 cm square. Its range was 11 bands, 0.479 cm apart, so the constant was 5461/0.479 or 11,400 A per cm. The position of a band could be read to about 0.01 wave length.

The procedure in making stress-optical measurements was the following: A sample on which measurements of dimensions had been made was mounted between the crossed nicols; the compensator was set with the central band on a cross hair (zero retardation), and its scale reading noted. The specimen was then stressed, by attaching to it a pan to which weights were added, and the compensator then adjusted to bring the central band on the cross hair, and the scale read. After the length between the reference marks on the specimen was read by means of the cathetometer, the compensator reading was again checked to ascertain whether optical creep had occurred. Successive additions of weight were made until optical creep was observed or until the sample broke, as happened with some of high sulphur content. The upper support which held the specimen was adjusted after each addition of weight to keep the constricted portion centered in the optical path. The pan was clamped before each addition of weight, and was released gently so as not to permit oscillation. No definite time schedule was followed in conducting the operations. The observations on a given specimen were usually made without interruption at 10 to 20 increasing stresses, and occupied about one to two hours. The temperature at which measurements were made was not controlled, but it was regularly observed and recorded.

IV. COMPUTATION OF COEFFICIENT OF RELATIVE RETARDATION, STRESS-OPTICAL COEFFICIENT, AND STRESS

The relative retardation per unit thickness is expressed by the relation,

$$\Delta n = \frac{R}{d},$$

[7] Holt, BS J. Research **10**, 575 (1933) RP549.

where R is the observed relative retardation, and d, the thickness in the same units. When the relative retardation is measured by means of the compensator mentioned above, and the thickness is found from the thickness in the unstressed state and the elongation, this equation becomes,

$$\Delta n = \frac{(11{,}400\ \Delta x)}{d_0}\sqrt{\frac{L}{L_0}}$$

where Δx is the change in setting of the compensator, 11,400, the compensator constant, L_0 and L, the original length and the length under stress, respectively, and d_0, the original thickness.

The stress-optical coefficient is defined by the relation,

$$C = \frac{R}{Td} = \frac{\Delta n}{T},$$

where C is the coefficient, and T, the tensile stress. The stress-optical coefficient has the dimensions of the reciprocal of a stress. When the relative retardation is expressed in Angstrom units, the stress in bars, and the thickness in millimeters, the stress-optical coefficient is given in brewsters.

The stress in bars was usually found from the relation,

$$T = 980.7 \times 10^{-6}\left(\frac{mL}{d_0 w_0 L_0}\right),$$

where T is the stress, m, the load in grams, and d_0 and w_0, the thickness and the width, in cm, respectively, of the sample in the unstressed state. This stress relates, of course, to the actual cross section, not the original cross section which is commonly used in connection with stress-strain curves for rubber.

This equation for the stress, as well as the one for the coefficient of relative retardation involves the assumption that the reduction in thickness and the reduction in width of a stressed specimen are each proportional to the square root of the increase in length. In the case of one compound, designated as B in table 1, this assumption was verified by direct measurements with the screw micrometer gage on a number of specimens. These measurements gave an average value for Poisson's ratio as 0.502 at elongations up to 350 percent. The amount by which this differs from 0.500 was less than the probable error of the determination.

Further evidence regarding Poisson's ratio may be adduced from measurements of the change of volume of rubber on stretching, provided the assumption is made that the ratio is the same in the thickness and in the width dimension. This latter assumption is reasonable in view of the well-known isotropic character of mold-cured rubber of the "pure-gum" type.

Measurements of the volume change on stretching were made on compounds B, D, F, and G.[8] None of these showed any appreciable change of volume at elongations up to 350 percent. At an elongation of 400 percent, compounds B and D decreased in volume by 1 or 2 parts per 1,000; at 500 percent, the decrease was 5 to 8 parts per 1,000; and at 600 percent, it was 10 to 15 parts per 1,000. Compounds F and G, on the other hand, showed no significant change of volume at 500 percent elongation, while at 600 percent the volume decreased by 1 to 2 parts per 1,000.

[8] Holt and McPherson, Unpublished work.

With the majority of the compounds the photoelastic measurements were terminated at elongations below 400 percent. Neglect of the volume change on stretching probably occasioned no appreciable error in the case of these compounds, or in the case of compounds F and G which were measured at elongations up to 550 or 575 percent. Compounds H and K were measured at elongations up to about 580 percent, but in the absence of definite data on the volume relations for these compounds no definite estimate can be made of the probable error entailed by neglecting the change of volume on stretching at the higher elongations. It was, however, probably not great.

V. RELATION OF COEFFICIENT OF RELATIVE RETARDATION AND STRESS-OPTICAL COEFFICIENT TO STRESS

When the retardation coefficients of the different rubber compounds were plotted against the stress, the relation was in some instances linear, while in other cases it showed a greater or less deviation from a linear function. It was found that the relations could be expressed by equations of the form,

$$\Delta n = aT + bT^2 + cT^3$$

where Δn is the retardation coefficient, T the stress, and a, b, and c are constants for any given rubber compound under specified conditions of measurement. For some compounds b and c are zero; the measurements on other compounds at stresses below about 65 bars are adequately represented by making c equal to zero, while at higher stresses c was not zero.

The coefficients, a, b, and c, of the above equation were determined for all the specimens investigated and are here employed as a means of presenting the results of the investigation in concise form. The values of the parameters are given in table 2, along with other data regarding the determinations, including the temperature at which the measurements were made, the range of stresses employed, and the corresponding elongations produced in the samples. The range of stress covered extended to between 50 and 100 bars in the case of most compounds, and to 164 bars in one instance. Values of the retardation coefficient ranged up to 100 to 200×10^{-4} in most instances.

Curves showing the relation of the coefficient of retardation to stress for a typical sample of each compound are presented in figure 1. The smooth curves were computed from equations using values of a, b, and c from table 2, while the points shown represent observations. In most cases the points cannot be distinguished from the curves on the scale of the figure. The differences, however, were computed, and are summarized in the last two columns of table 2. The average discrepancies range from 0.1 to 0.45×10^{-4} unit of the retardation coefficient for the different compounds, while the maximum discrepancies are from 0.25 to 2.0×10^{-4}. These relate to values of the retardation coefficient ranging up to 100 or 200×10^{-4}. The results obtained with specimens of compounds G and H are expressed by second-degree equations at stresses below 65 bars, and by third-degree equations for the complete range of observations which extend to about 100 bars. The second-degree equations were found in order that the parameters a and b might be correlated with the composition, as is discussed in a subsequent part of this paper.

TABLE 2.—*Summary of photoelastic measurements*

Compound	Sample number	Temperature	Range of elongation	Range of stress [1]	Parameters of equation,[2] $\Delta n = aT + bT^2 + cT^3$			Difference between values of Δn (obs.) and Δn (calc.) $\times 10^4$	
					$a \times 10^4$	$b \times 10^4$	$c \times 10^4$	Max	Avg
		° C.	Percent	Bars					
A	1	26.1	26 to 308	2.78 to 45.65	2.059	0	0	0.5	0.2
	2	27.7	26 to 324	2.77 to 51.1	2.044	0	0	.4	.2
	3	30.5	25 to 299	2.78 to 44.95	2.019	0	0	.85	.3
B	1	24.0	26 to 323	2.73 to 55.0	2.092	0	0	.4	.1
	2	25.5	25 to 335	2.95 to 54.3	2.092	0	0	.4	.15
	3	24.2	25 to 260	2.95 to 38.6	2.097	0	0	.3	.15
	4	22.4	13 to 261	1.68 to 40.0	2.108	0	0	.7	.2
	5	27.8	14 to 273	1.69 to 41.15	2.084	0	0	.5	.2
	6	24.0	25 to 258	2.96 to 39.5	2.091	0	0	.6	.2
	7	22.5	6 to 129	0.73 to 15.65	2.108	0	0	.2	.05
C	1	24.0	13 to 308	1.76 to 63.2	2.233	−0.00354	0	.3	.15
D	1	28.8	31 to 365	2.70 to 44.6	2.158	0	0	.7	.15
	2	24.4	33 to 348	2.82 to 40.45	2.155	0	0	.8	.25
E	1	----------	30 to 365	2.72 to 49.4	2.267	−0.00175	0	.3	.15
	2	24.5	30 to 362	2.75 to 49.65	2.242	−0.00146	0	.3	.15
F	1	26.9	69 to 572	3.87 to 65.2	2.660	−0.00820	0	.3	.1
G	1	21.8	40 to 470	2.91 to 65.0	2.895	−0.01000	0	.65	.25
	1	21.8	40 to 556	2.91 to 96.95	2.895	−0.01127	0.000023	1.3	.45
H	1	25.6	30 to 403	2.84 to 64.2	3.120	−0.01075	0	.95	.35
	1	25.6	30 to 506	2.84 to 109.5	3.120	−0.01258	0.000029	.6	.3
	2	31.7	34 to 582	3.29 to 163.6	2.988	−0.01170	0.000026	1.95	.45
I	1	27.2	27 to 380	2.92 to 74.15	3.297	−0.01138	0	.75	.4
	2	27.3	27 to 383	2.95 to 74.6	3.275	−0.01110	0	.8	.3
J	1	27.9	19 to 345	2.20 to 68.5	3.509	−0.01216	0	.75	.35
K	1	26.0	58 to 581	3.41 to 68.4	3.005	−0.00909	0	.7	.3
L	1	25.3	32 to 296	2.83 to 35.95	3.531	−0.01313	0	.25	.1
M	1	25.0	31 to 142	3.57 to 17.3	4.108	−0.01466	0	.25	.1

[1] Stress refers to actual cross section.
[2] Δn is relative retardation per unit thickness, and T, stress.

Measurements on specimens of compounds A and B were made at temperatures covering ranges of 4° or 5°. The results indicate a decrease in retardation coefficient of the order of 0.25 to 0.5 percent per

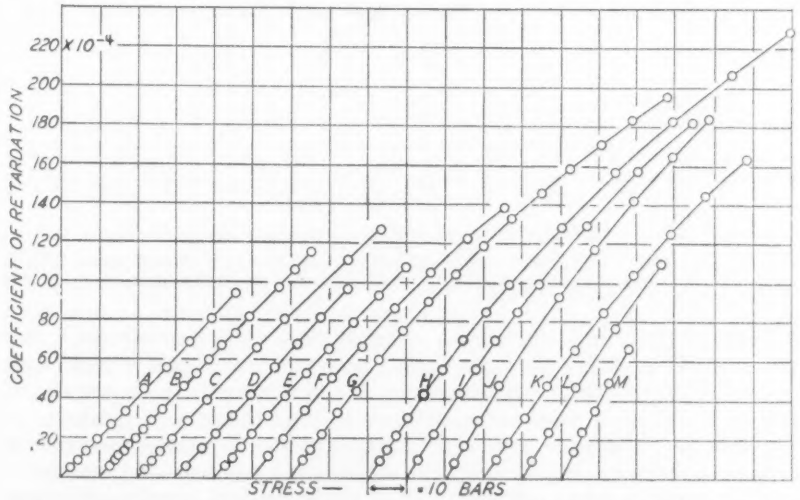

FIGURE 1.—*Relation of coefficient of relative retardation to tensile stress.*

Compounds A to E represent rubber compounds made with organic accelerators, F to J, compounds of crude rubber and sulphur, K to M, compounds of purified rubber and sulphur. Each curve is plotted from a separate origin to avoid confusion. The stress relates to the actual cross section.

degree, but are not sufficiently precise to warrant the computation of temperature coefficients.

Stress-optical coefficients were found corresponding to all measurements of retardation coefficient. The coefficients for typical samples of the various compounds are shown in figure 2, plotted as functions of the stress. The smooth curves were found by means of the values for the parameters, a, b, and c, given in table 2, while the points shown represent observations. In the case of compounds A, B, and D, the coefficient is constant and independent of stress. In the case of other compounds, the values for the coefficient decrease with increasing

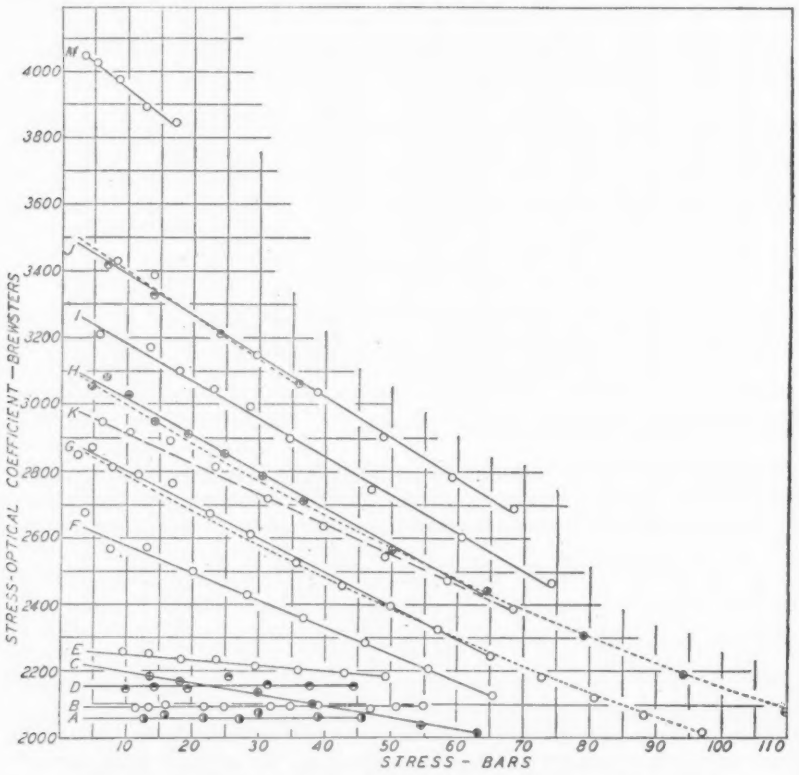

FIGURE 2.—*Relation of stress-optical coefficient to tensile stress.*

Curves for compounds J and L almost coincide; the dotted curve refers to L. The solid curves for compounds G and H were computed from equations in a and b, the dotted curves from equations in a, b, and c. The stress relates to the actual cross section.

stress, the slopes and intercepts varying with the compound. For compounds G and H, straight lines, in terms of a and b represent fairly well the results at stresses below 65 bars; these are shown in the figure by solid curves. Measurements on these compounds at higher stresses, however, are well fitted only by equations in terms of a, b, and c, which are represented in the figure by the dotted curves.

At low stresses the values for the stress-optical coefficient show considerable scattering, for the reason that they represent the ratios of small values of the retardation coefficient and stress, and hence are not of high precision. In the figure the points at stresses below 10 bars have been omitted from some of the curves, to avoid confusion.

The numerical values of the stress-optical coefficient for the compounds made with accelerators all fall between 2,000 and 2,300 brewsters. For rubber-sulphur compounds at low stresses, the values are from about 2,600 to 4,100 brewsters, but these decrease with increasing stress, and at relatively high stresses drop to as low as 2,000 brewsters.

VI. RELATION OF THE PHOTOELASTIC PROPERTIES OF RUBBER TO THE COMPOSITION

The examination of the results presented in the previous section indicates that the rubber compounds fall into three groups as regards

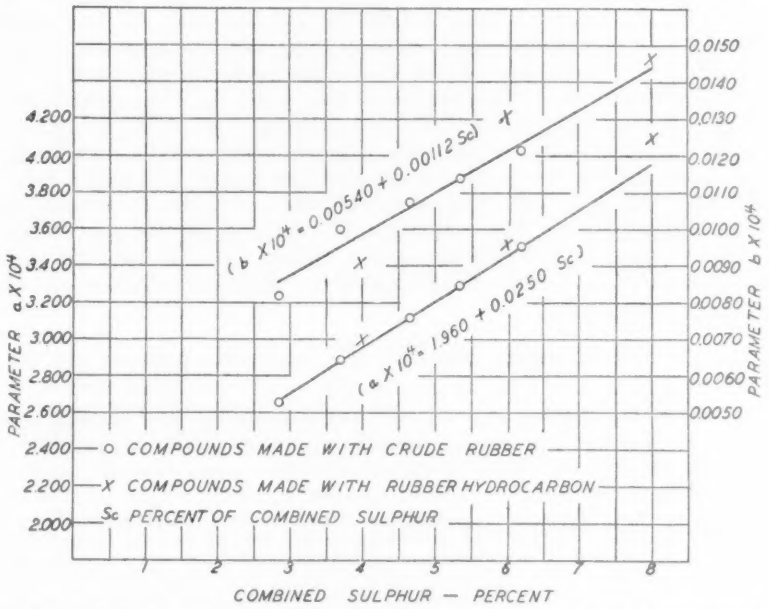

FIGURE 3.—*Relation of parameters a and b to percentage of combined sulphur in rubber-sulphur compounds.*

The parameters are the coefficients in the equation, $\Delta n = aT + bT^2$, where Δn is the coefficient of relative retardation, and T the tensile stresss. Values of b shown in the figure are negative in sign.

photoelastic properties. In one group are the compounds A, B, and D for which the parameters b and c are zero, the relation of coefficient of retardation to stress is linear, and the stress-optical coefficient is constant. A second group is made up of compounds from F to M, inclusive, for which the parameter c is either zero or has a small positive value while the parameter b has a relatively large negative value, indicating that the relation of the coefficient of retardation to the stress departs considerably from a straight line, and that the stress-optical coefficient decreases markedly with increasing stress. The third group is made up of compounds C and E, which fall between the two previous groups in respect to photoelastic properties.

This division into groups follows the mode of vulcanization. Compounds A, B, and D are vulcanized with the aid of organic accelerators, employing the minimum percentages of sulphur con-

sistent with the development of good physical properties. Compounds F to M, inclusive, on the other hand, are rubber-sulphur compounds vulcanized without the aid of organic accelerators, while compounds C and E contain accelerators, but also contain more sulphur than the minimum required to develop good physical properties, and hence partake of the character of both the rubber-sulphur and the accelerated compounds.

When the measurements on the rubber-sulphur compounds are expressed in equations of the second degree, the parameters a and b both bear approximately linear relations to the combined sulphur content, as is indicated by the curves shown in figure 3. The points representing measurements on compounds containing rubber hydrocarbon are distinguished in the figure from those on compounds containing crude rubber; they might be represented by two slightly different curves, but this has not been done because data are available on only three compounds of the rubber hydrocarbon, and are not considered adequate to define an exact relation. One straight line was drawn through values of a for the compounds F to J, inclusive, and another straight line through the corresponding values of b. These lines represent, with reasonable fidelity, the values of a and b for compounds K and L, but are somewhat too low in the case of compound M.

The equations for the relations of a and b to the percentage of combined sulphur are shown on the figure. These lead to the following expression for the coefficient of relative retardation of rubber sulphur compounds,

$$\Delta\ n\times 10^4=(1.960+0.0250\ S_c)\ T-(0.00540+0.00112\ S_c)\ T^2$$

where S_c is the percentage of combined sulphur and T, the tensile stress. This relation is applicable to compounds containing 2.85 to 6.2 percent of combined sulphur, and to measurements at stresses up to 65 bars.

WASHINGTON, October 12, 1934.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP752

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AN ANALYSIS OF CONTINUOUS RECORDS OF FIELD INTENSITY AT BROADCAST FREQUENCIES[1]

By Kenneth A. Norton, Samuel S. Kirby, and Gordon H. Lester

ABSTRACT

Continuous records of the field intensities of most of the broadcasting stations in the United States have been made at the National Bureau of Standards receiving station near Washington, D. C. Typical records of received field intensities from several stations are presented. Maximum field intensities during 10-minute time intervals are analyzed in the following ways to illustrate sky-wave propagation phenomena at broadcast frequencies for distances up to 4,000 kilometers. (1) The diurnal variation of the 10-minute maxima is given for several stations. (2a) The variation of the 10-minute maxima is shown with respect to distance for night field intensities. (2b) These variations are also shown for sky waves received during the daytime. Empirical formulas are developed to represent the data of (2a) and (2b). The data are explained in terms of a theory of propagation of waves in the ionosphere.

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During the past 3 years graphical records of the field intensity of over 300 broadcasting stations in the United States and Territories have been made at the National Bureau of Standards receiving station at Meadows, Md., near Washington, D. C. The method used for recording the field intensity is described elsewhere.[2] It is the purpose of this paper to report these data and some of the conclusions reached from an analysis of these records.

I. EXPERIMENTAL DATA

In order to illustrate the type of field intensity record obtained and some of the general characteristics of the phenomena under consideration, some typical records are given of the received field intensity from broadcasting stations WLW in Cincinnati, Ohio, and WCKY in Covington, Ky. The upper record in figure 1 shows the received field intensity of WLW as measured at the Meadows field station (lat. 38°48′32″ N., long. 76°52′40″ W.). From 6 a.m. to 1 a.m. the power used was 50 kw and from 1 a.m. to 5:30 a.m. the power used was 500 kw. It is evident from the records that transmissions were stopped intermittently between 2 a.m. and 6 a.m. The

[1] Presented at the Ninth Annual Convention, Institute of Radio Engineers, Philadelphia, Pa., May 27 to 30, 1934, and at General Assembly, International Scientific Radio Union, London, England, Sept. 12 to 18, 1934.

[2] K. A. Norton and S. E. Reymer. BS J. Research 11, 373 (1933) RP597.

inverse distance values were calculated on the assumption that these indicated amounts of power were actually radiated. The maximum received field intensities reach values 2½ times the inverse distance field intensities. The fading observed throughout the daytime indicates a received sky wave of intensity comparable to that of the ground wave since ground-wave field intensities are free from fading. In order to indicate the relative intensity of this station the intensities of the ground waves of the four local Washington stations are shown: WMAL, 630 kc/s, 500 w, 14 km; WRC, 950 kc/s, 500 w, 19 km; WJSV, 1,460 kc/s, 10 kw, 15 km behind directional antenna; WOL, 1,310 kc/s, 100 w, 17 km. On the lower record 500 kw was used throughout the day. The peak field intensity was only 17 mv/m on this day as compared to 25 mv/m a week earlier. Such a variation is typical of night field intensities at broadcast frequencies. The period of the night fading at this frequency is about 5 minutes.

Figure 2 shows two records of WCKY, the upper record for June 23 near the summer solstice and the lower record for December 20 near the winter solstice. The most conspicuous difference between the two records is the absence of any recordable field intensity during the summer day and the relatively strong sky wave present during the winter day. The peaks which may be seen during the summer day represent interference from other stations, only a weak beat note being audible for WCKY. The noise level at night is about eight times as strong in the summer. Also the night field intensities are about twice as strong in the winter record. Notice particularly the night fading at this frequency which has a period of about 1½ minutes. The record from midnight to 7 a.m. represents atmospherics.

In order to condense the enormous amount of data obtained, our records were analyzed in terms of the peak field intensities which were observed during 10-minute intervals. It may be mentioned that the average of six consecutive 10-minute maxima corresponds closely to the quasi-maximum field intensity for the hour, i. e., the field intensity which is exceeded during the hour only 5 percent of the time. In order to make some correction for the power it was assumed that each station radiated one-half of its rated power. Admittedly this was a very poor assumption but it was about the best that could be done in view of the fact that for most stations the amount of power which is radiated is not known. As an illustration of how poor this assumption regarding radiated power may be in some cases it may be mentioned that WLW with a rated power of 500 kw actually radiates at low angles power equivalent to 870 kw for the ordinary vertical distribution assumed for other stations. The usual formula for the radiated power for a vertical infinitesimal doublet is used in these calculations, i. e., $P_r = \frac{F^2 D^2}{C^2}$ kw, where F is the measured ground wave field intensity in microvolts per meter at a distance D in kilometers, and C is the velocity of light in kilometers/second. In the few cases where field intensity measurements had been made near the station, the radiated power was calculated by means of the above formula in terms of these measurements. Such cases were the exception rather than the rule and still do not take into account the radiation characteristics in the vertical and horizontal planes.

Figure 3 shows the diurnal variation of the 10-minute maxima for several clear-channel broadcasting stations. They are shown on a

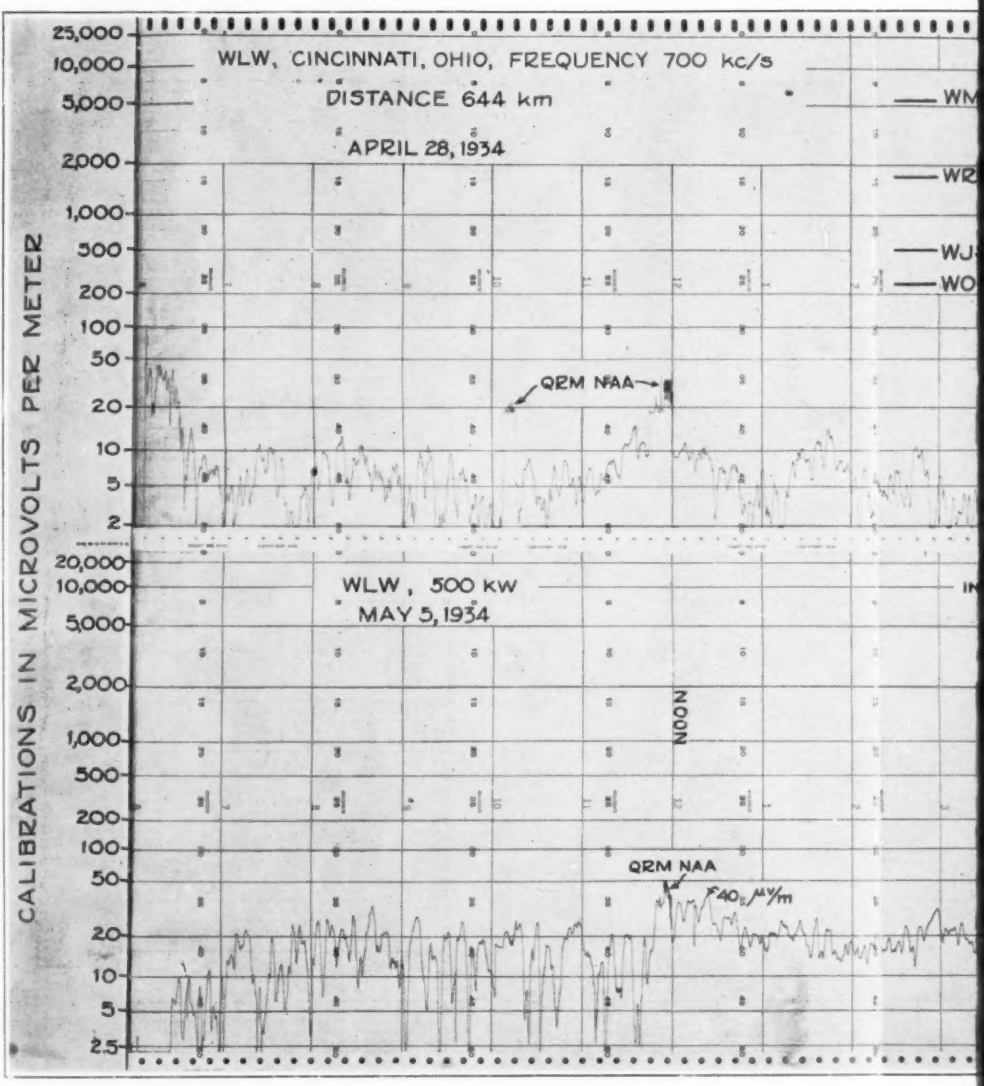

WLW, CINCINNATI, OHIO, FREQUENCY 700 kc/s
DISTANCE 644 km
APRIL 28, 1934
QRM NAA
WLW, 500 kW
MAY 5, 1934
NOON
QRM NAA
40 μv/m
CALIBRATIONS IN MICROVOLTS PER METER
25,000
10,000
5,000
2,000
1,000
500
200
100
50
20
10
5
2
20,000
10,000
5,000
2,000
1,000
500
200
100
50
20
10
5
2.5

FIGURE 1.

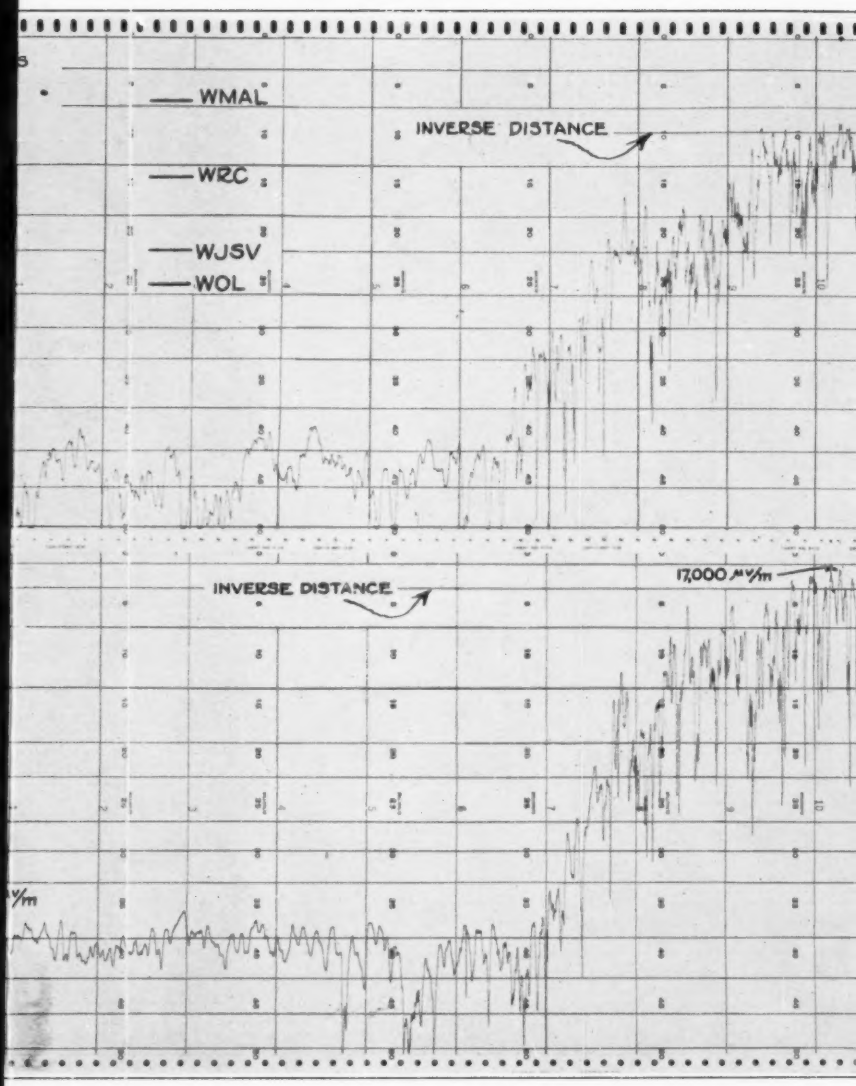
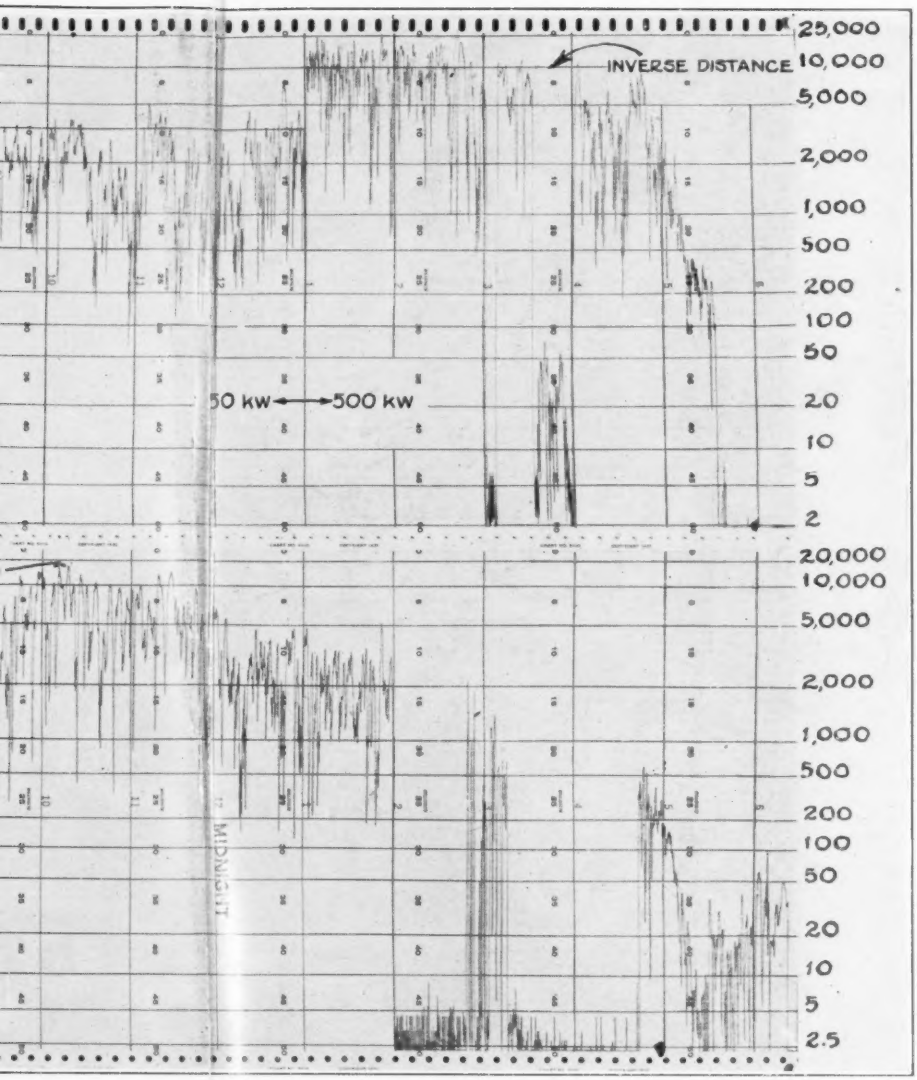


FIGURE 1.—*Graphical field intensity record of WLW, Cincinnati, Ohio.*



Ohio.

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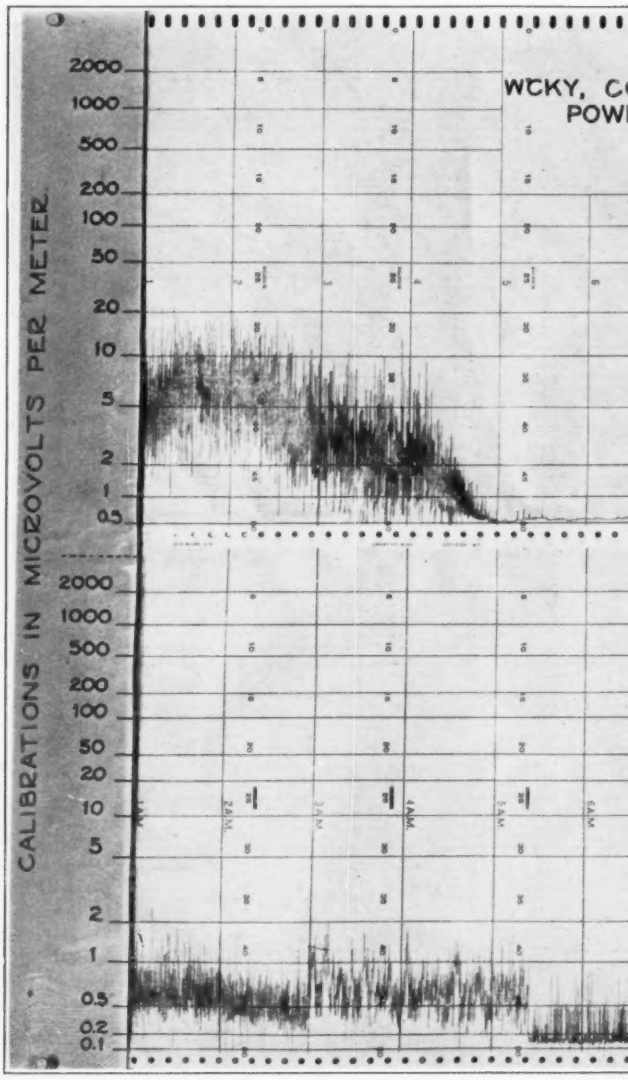

WCKY, C
POW
CALIBRATIONS IN MICROVOLTS PER METER
2000
1000
500
200
100
50
20
10
5
2
1
0.5
2000
1000
500
200
100
50
20
10
5
2
1
0.5
0.2
0.1

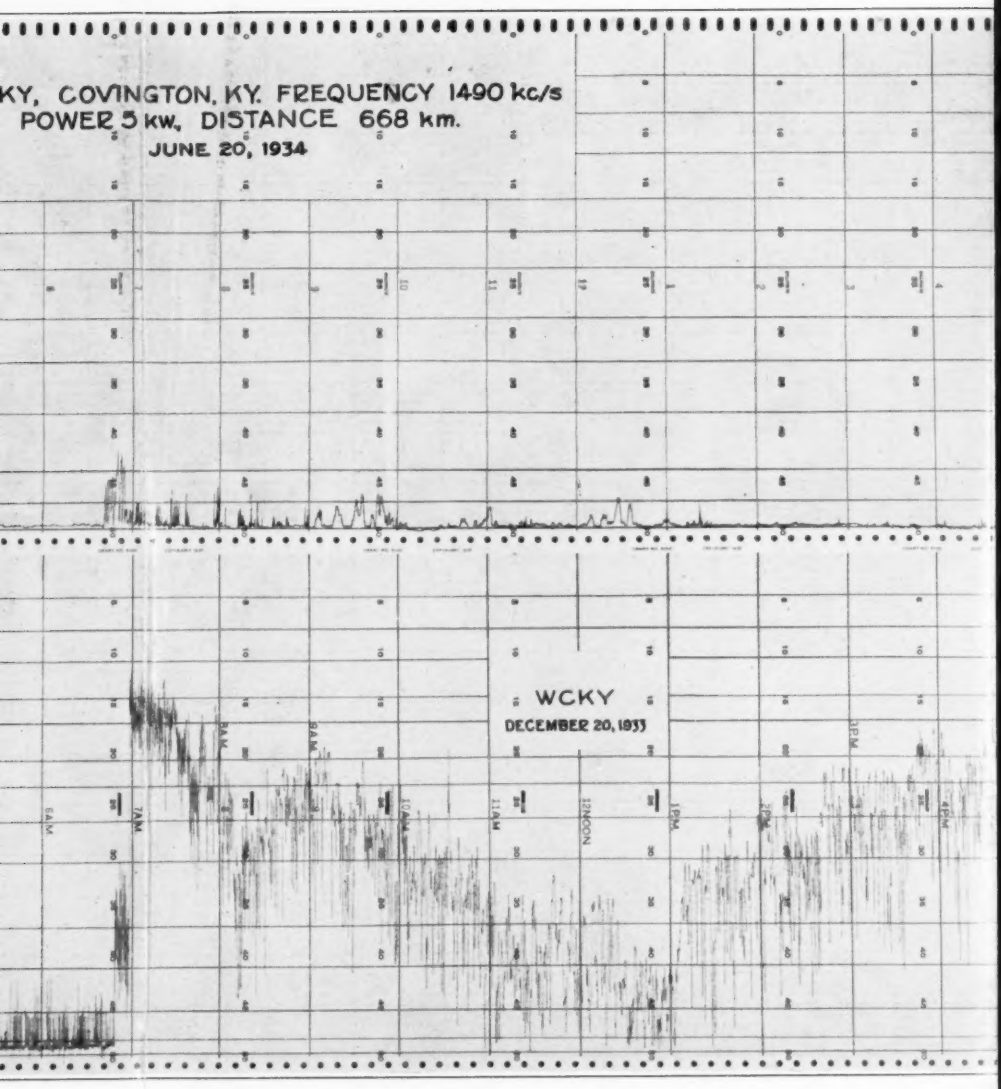
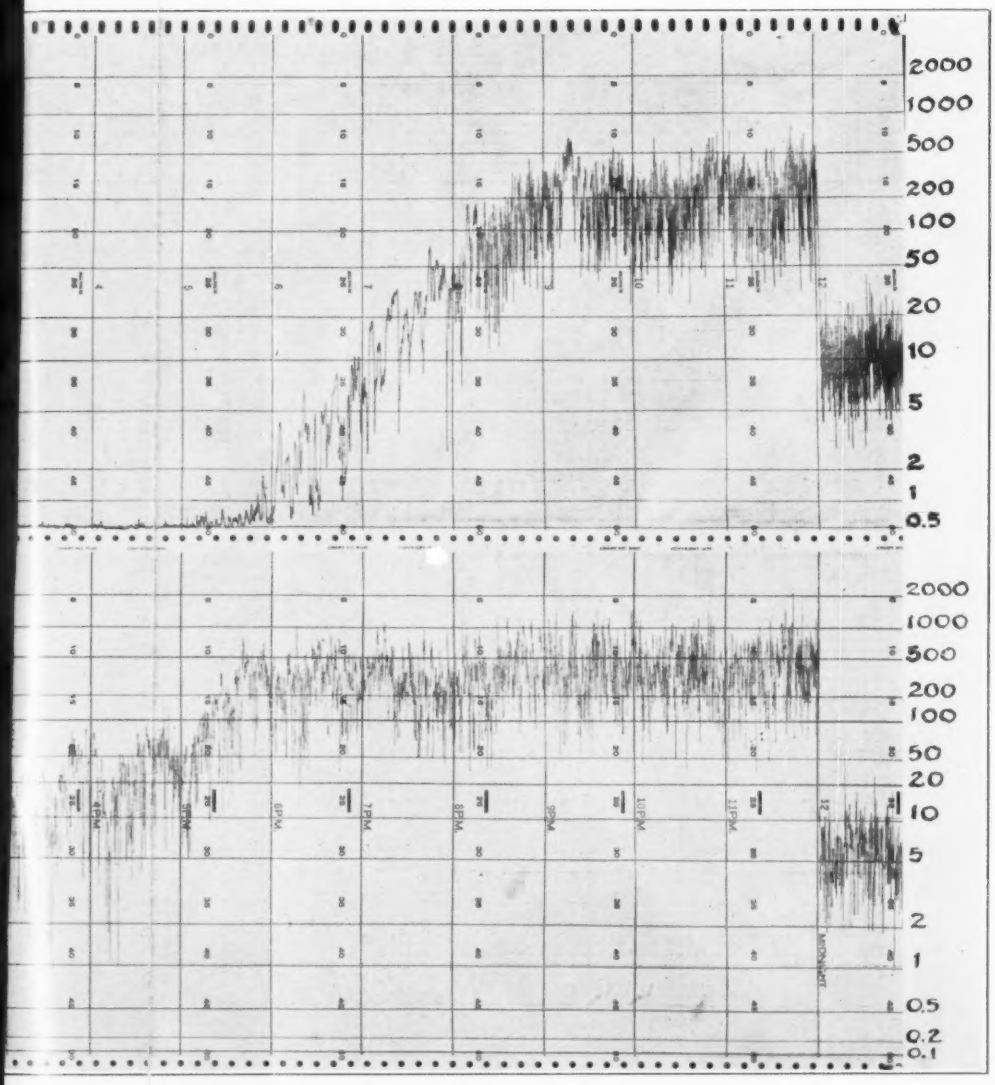


FIGURE 2.—*Graphical field intensity record of WCKY, Covington, Ky.*



Covington, Ky.

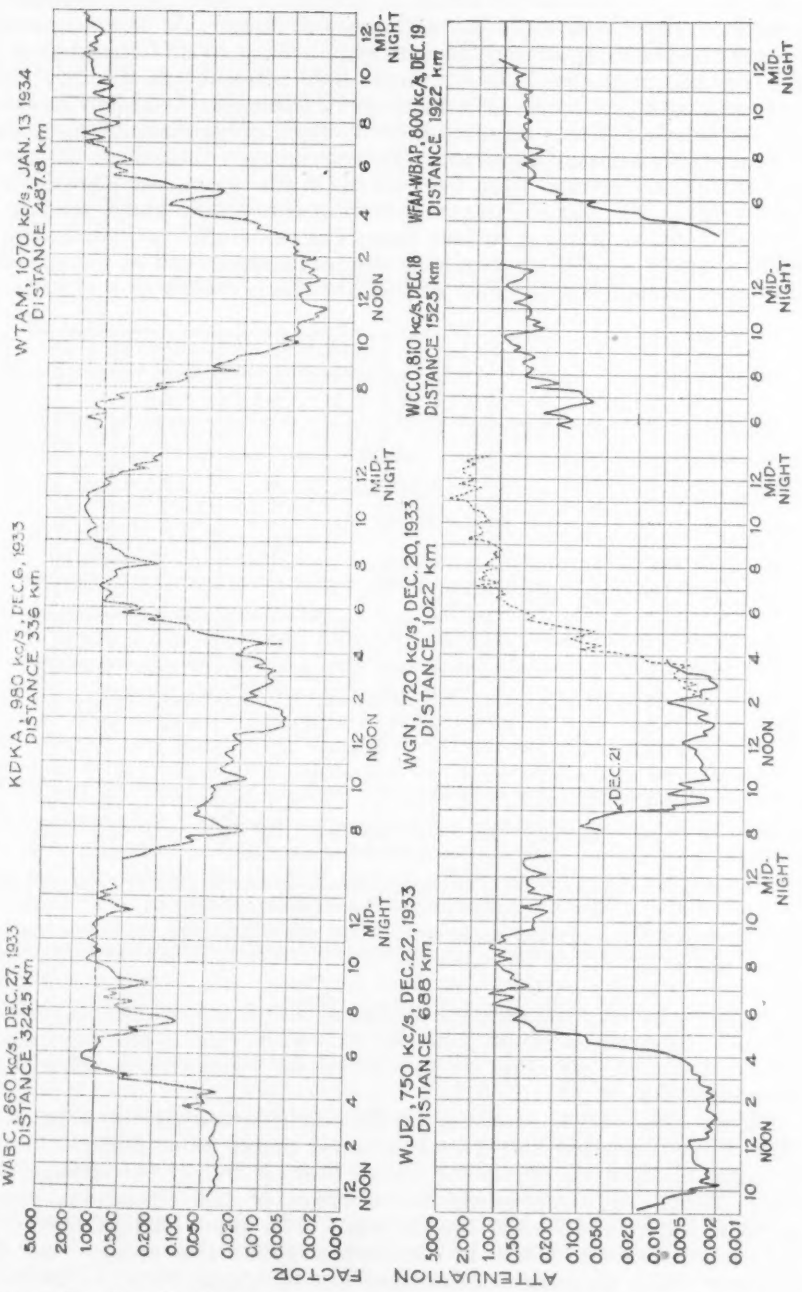


FIGURE 3.—*Sample diurnal variations of the attenuation factors of several broadcasting stations given as a function of distance.*

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logarithmic scale with the calculated inverse distance field intensity equal to one. If we write $F=AC\sqrt{P_r}/D$, then each measurement of field intensity determines an attenuation factor, A; these are the values plotted in figure 3. The principal thing to be noticed here is the increase in the ratio of the night field intensity to the day field intensity with distance. The increase in this ratio is evident in spite of the fact that it was impossible to keep all of the variables such as frequency and terrain constant. It may be seen that these attenuation factors are greater than 1 for all the stations at some time during the evening, the highest peaks occurring for WGN which reaches a peak of 4, corresponding to four times the calculated inverse distance field intensity. Of interest also is the fading observed at the greater distances during the daytime indicating the presence of a sky wave

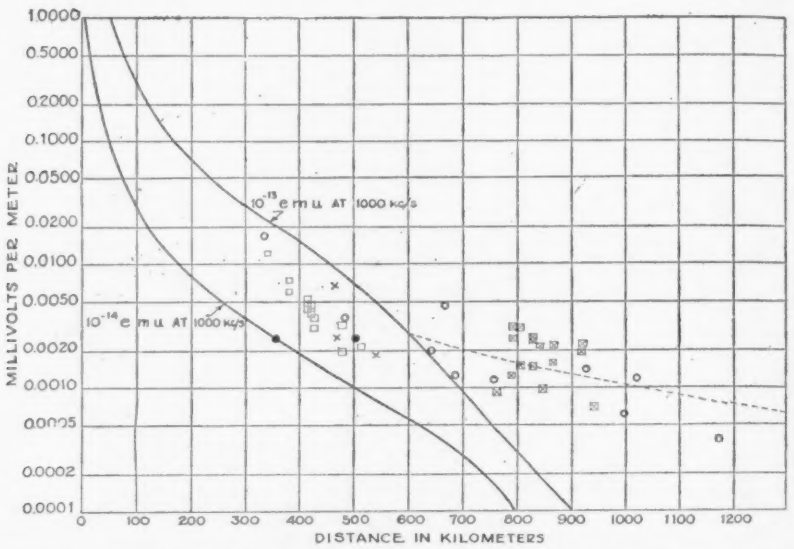

FIGURE 4.—*Daytime field intensity measurements reduced to 1* kw *of radiated power and given as a function of distance for broadcasting stations in the U. S. A.*

The solid curves were taken from the Report of the U. S. Committee on Radio Propagation Data and are theoretical ground-wave formulas. The dotted curve represents an empirical formula for distances greater than 600 km.

of intensity at least comparable to that of the ground wave. Evidence will now be given to show that this sky wave during the daytime is much stronger than the ground wave for distances greater than about 600 km.

Figure 4 shows the received daytime field intensities for a number of stations corrected to 1 kw of radiated power as a function of the distance at those distances for which there is fading throughout the day. Each point represents the average of the 10-minute peaks received between 10 a.m. and 2 p.m. The open circles represent our measurements made in December 1933, the crosses are for January 1934, and the solid circles are for April 1934. The solid lines indicate the theoretical variation of the received field intensity of the ground wave at 1,000 kc/s for 10^{-13} and for 10^{-14} electromagnetic units conductivity as taken from the Report of the U. S. Committee

on Radio Propagation Data.[3] The boxes represent measurements made on WLW by their engineers. The open boxes are for measurements east of WLW and the boxes with crosses are for measurements northeast of WLW. All of the measurements of WLW were made in February and March 1934, when snow was on the ground. It is probable that the received field intensities at distances greater than about 600 km are primarily due to sky waves since the variation with distance departs from the theoretical ground wave curves at these distances.

It was found that the empirical formula:

$$F=\frac{1{,}000\sqrt{P_r}}{D^2}(D>600 \text{ km, winter day}) \qquad (1).$$

fits the winter data satisfactorily for distances greater than 600 km This formula is shown dotted in figure 4. It may be mentioned that the daytime field intensity of WLW at 644 km and on 700 kc/s does not change much with season, while the daytime field intensity of WCKY at 688 km and on 1,490 kc/s is at least 100 times as strong during the winter day as for the summer day. It may be mentioned that the sky wave formula 1 agrees with the Sommerfeld ground wave formula at great distances for values of conductivity $\sigma_{emu}=4f^2\cdot 10^{-20}$ where f is the frequency in kc/s, i. e., for a conductivity of 10^{-14} electromagnetic units at 500 kc/s or a conductivity of 10^{-13} electromagnetic units at 1,600 kc/s.

In figure 5 the measured night field intensities are shown for about 300 stations as a function of the distance from the transmitter. Most of these measurements were made after 2 a. m. during the Federal Radio Commission's frequency monitoring schedules. Each point represents the maximum during a 10-minute time interval or the average of several such maxima but never more than six corresponding to an hour. There is one point for each separate night that the station was observed. They were corrected for power so as to correspond to 1 kw of radiated power. It will be observed that many of the maxima exceed the calculated inverse distance field as was evident also on the diurnal characteristics. Some of this excess is possibly due to too low an estimate of the radiated power but it is believed that part of it is real and may be explained on the assumption that several sky waves combine to give the observed maxima. Measurements were also made on two stations in Honolulu, Hawaii, at a distance of 7,775 km: KGU, 750 kc/s, 0.0011 mv/m per kilowatt on April 3, 1934; KGMB, 1,320 kc/s, 0.0037 mv/m per kilowatt on April 3, 1934, and 0.0076 mv/m per kilowatt on January 2, 1934. These points lie about the same distance below inverse distance as those near 4,000 km. The irregular curve shows the variation of night field intensity with distance as determined by a running average [4] of the data for distances less than 4,000 km. The general shape of this curve with a rise between 400 and 1,000 km is characteristic of broadcast transmission at night. The data obtained during the months of December 1933, January, February, and April 1934, were analyzed by months and no

[3] Proc. I. R. E., **21**, 1419 (Oct. 1933).

[4] The data were ordered according to distance. The field intensities for the first 10 distances were averaged to give an average field intensity for the distance corresponding to the average of the first 10 distances. The next average value of field intensity was determined by averaging the 4th to the 13th measured value of field intensity, etc. Since one application of this moving average process did not result in a sufficiently smooth curve, the process was repeated once to give the curve plotted in figure 5.

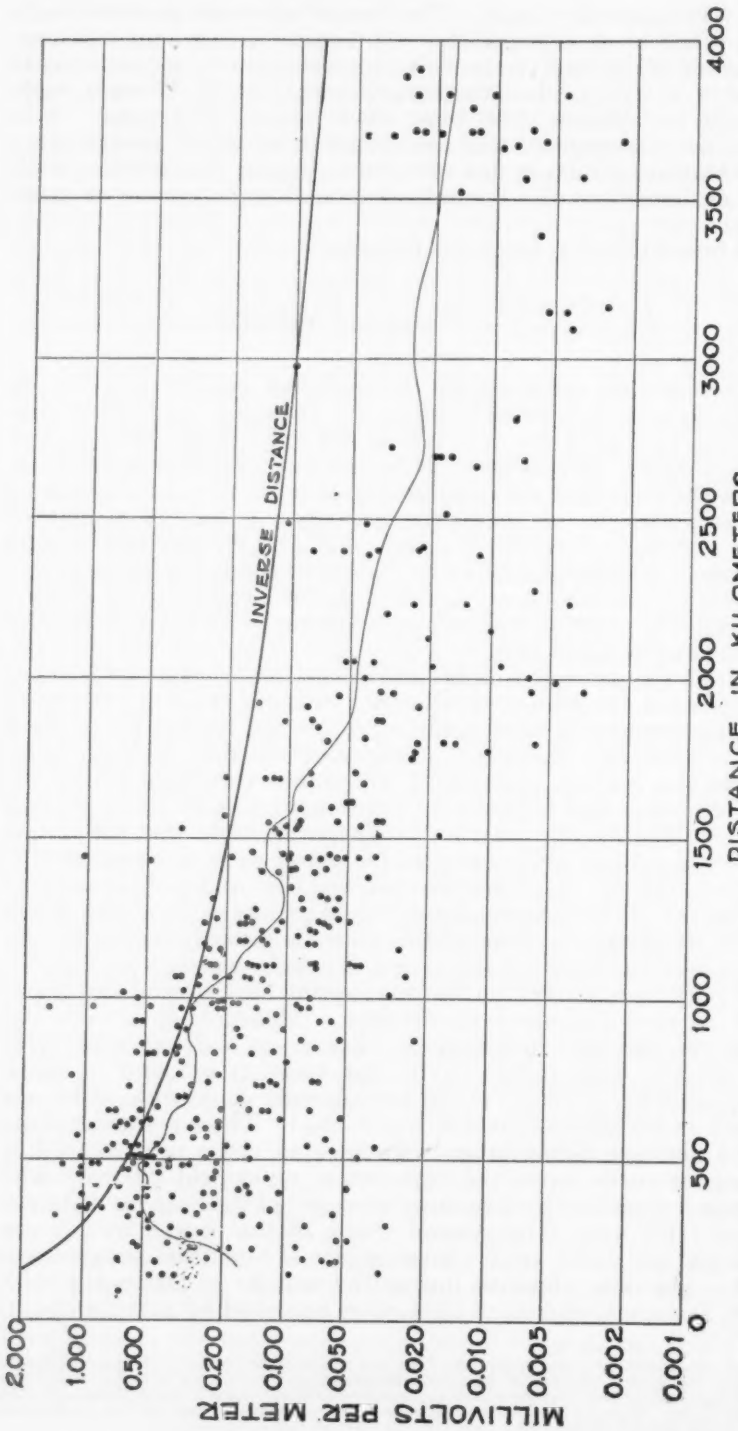

FIGURE 5.—*Night field intensity measurements reduced to 1* kw *of radiated power and given as a function of distance for the broadcasting stations in the U. S. A.*

The irregular curve represents a running average of the data.

significant difference was found. However, as summer approached, the measurements were less reliable on account of the high atmospheric noise level, consequently small differences could not be determined. Continuous 24-hour records of the field intensity as received at Meadows, Maryland, of stations WEAF in New York, are available for a period of over a year. Similarly, records are available for WCKY in Covington, Ky., for over a year and for WLW for a period of greater than 6 months. These records are now being analyzed to determine samples of the seasonal variations at broadcast frequencies. Similarly, the data were analyzed for four different frequency ranges in the broadcasting band and no significant changes with frequency were found. Thus it may be concluded that there is no large variation of night field intensity with season or frequency for the range from 550 to 1,500 kc/s.

It was found that the empirical formula:

$$F = C\sqrt{P}\,\frac{1{,}600 + D}{4{,}410{,}000 - 11{,}000D + 10D^2} \text{ (night sky wave)} \qquad (2)$$

fits the averaged data satisfactorily. This formula, together with the averaged data, is shown in figure 6. The maximum sky wave field intensity predicted by formula 2 occurs at 580 km.

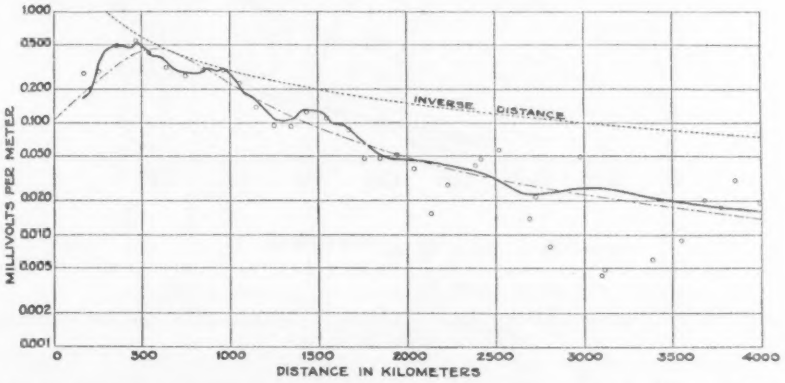

FIGURE 6.—*Two averages of night field intensity measurements together with the graph of an empirical formula which was designed to represent the data.*

The points plotted in figure 6 were obtained by an independent method of averaging and give credence to the major humps at 500, 1,000, and 1,500 km which were exhibited by the running average of the data. Each point represents the average of the measured field intensities in a 100-km interval of distance plotted at the average distance in the interval. The 0 to 100, 3,200 to 3,300, and 3,400 to 3,500 km intervals contained no measurements; the maximum number of measurements per 100-km interval was 30 which were made in the 1,100 to 1,200 km interval.

II. A THEORETICAL EXPLANATION OF THE DATA

Two simple theories of the attenuation of radio waves in the ionosphere were developed. The details of these theories are given in the appendix. The attenuation was calculated from these theories and an average polar diagram (i. e., $\sqrt{P_r(\psi_1)}$ see eq 23) was then calculated from the averaged field intensity data given in figures 5 and 6. Figure 7 shows two polar diagrams thus calculated. It should be emphasized that these represent the average polar characteristic of all the transmitting antennas multiplied by the polar characteristic of the receiving antenna. The receiving antenna was a vertical wire less than a quarter wave length long. The dotted graph was determined by setting $k=0$ in eq 23 on the assumption that the waves were reflected without absorption at a layer 100 km high; i. e., on the

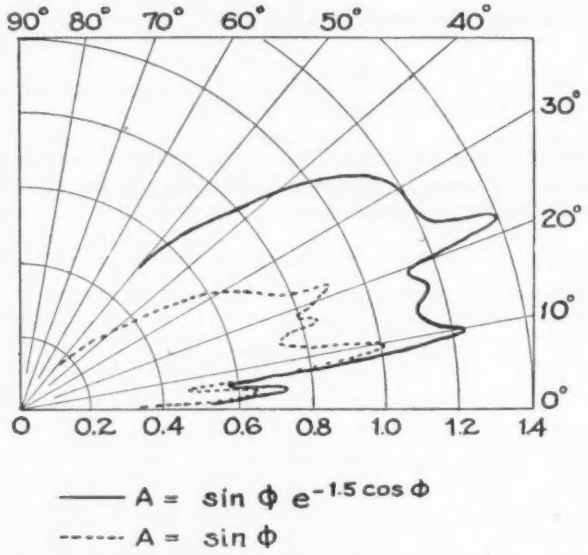

FIGURE 7.—*Theoretical average polar radiation characteristics for broadcasting stations in the U. S. A.*

assumption that the attenuation was due only to the fact that the wave traveled to a 100-km layer and back. This assumption corresponds for the purpose of our analysis to that used by P. P. Eckersley [5] and later by Stuart Ballantine [6] and gives an attenuation factor $A=\sin \phi_1$ where ϕ_1, denotes the angle of incidence at the layer. (See Appendix I.) The amount of radiation above 45 degrees (see dotted curve, fig. 7) which is calculated on this assumption is hardly as much as might be expected from the average transmitting antenna in use by the stations measured. The solid curve in figure 7 was calculated from the average data on the assumption that the waves were refracted back to earth at a 100-km layer in which the ion density varied exponentially with the height. This assumption gives an attenuation factor independent of the frequency and equal to $\sin \phi_1 e^{-k \cos \phi_1}$. (See Appendix II.) The constant k was arbitrarily

[5] Proc. I. R. E., **18**, 1160 (July 1930).
[6] Proc. I. R. E., **22**, 619 (May 1934).

taken to be 1.5. It is evident that a larger amount of high-angle radiation is obtained with an attenuation factor of this form and the relative amount may be changed further by an adjustment of the constant k. Since the solid curve in figure 7 has approximately the general shape which might be expected for $\sqrt{P_r(\psi_1)}$, we are led to believe that formula 23 properly relates the variables influencing sky-wave propagation in the broadcasting band at night. The constant k, being theoretically proportional to the average collision frequency of the ions along the ray path, may very reasonably be expected to vary in a large measure from night to night since small changes in k might cause large changes in the pressure and thus in the collision frequency. This will explain the fact that field intensity observations on the same station at a fixed distance vary enormously from night to night. This probable variation in k may also be offered as a partial explanation of

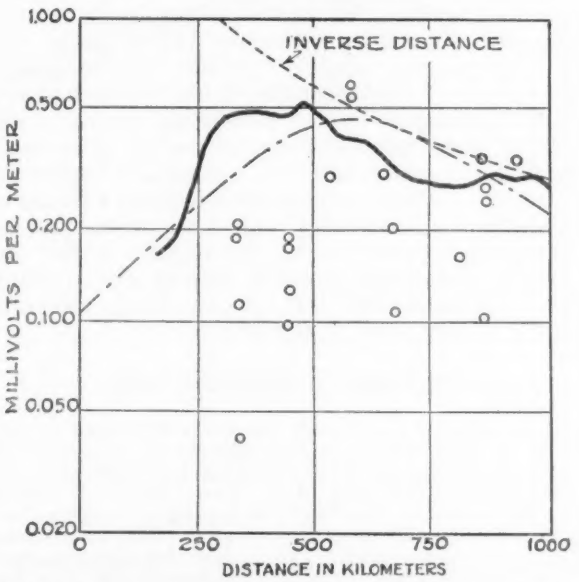

FIGURE 8.—*Night field intensity measurements of* WLW *compared to averaged data for other broadcasting stations in the U. S. A.*

the large variation of the data in figure 5 above and below the averaged data; the remainder of this variation is probably due to a variation of $P_r(\psi_1)$ for the different stations measured.

For distances greater than about 2,000 km the field intensities are received after two or more reflections since the curvature of the earth shields the receiver from the first reflection. At these distances also the refraction theory gives a more adequate explanation of the data, the simple reflection theory tending to predict too large values of received field intensity.

After the recent installation of the new 500-kw transmitter for WLW, their engineers made many field-intensity measurements. Figure 8 shows the results of several sets of measurements after they were corrected for radiated power. Each point represents the maximum field intensity observed at a given location. The period of observa-

tion for each of these points varied from about 5 min to about 5 hr. A loop antenna was used for reception. These data are in good agreement with our own at the greater distances. The low values observed between 300 and 500 km are probably caused by the low-angle radiator (0.58λ vertical antenna) used by this station. Thus in the single case where we have measurements at various distances on a station for which we know the radiated power we obtain good agreement quantitatively with our averaged data or empirical formula 2 and qualitatively with our theory.

In conclusion we may enumerate the deductions made from the analysis of the data. Received night field intensities are often greater than inverse distance, reaching their maximum values at about 600 km. The average night field intensity for the average broadcasting station may be predicted by means of formula 2, but the individual measurements on a station may be expected to vary by a factor of 10 above or below its average. There are no large variations of received field intensity with season or frequency although, in general, the received field intensity is slightly weaker in the summer. The variation of the received field intensity at night with distance appears to be determined primarily by the directional characteristics in the vertical plane of the transmitting and receiving antennas. The theoretical formula 23 seems to give an adequate explanation of the data, the variation of $P_r(\psi_n)$ giving an adequate explanation of the variation of received field intensity with distance and the variation of k giving a plausible explanation of the night-to-night and diurnal variations. Field intensities received during the daytime at distances greater than about 600 km are sky waves and may be predicted during the winter time by formula 1.

APPENDIX I. REFLECTION

It is assumed in deriving this theory for the attenuation of sky waves at broadcast frequencies that the waves are reflected or refracted back to earth from a layer in the ionosphere of virtual height 100 km. The term virtual height is defined in papers by G. Breit and M. A. Tuve,[7] and T. R. Gilliland, G. W. Kenrick, and K. A. Norton.[8] The theory is applied by making the further assumption that the primary portion of the energy reflected back to earth reaches the receiver after only a single reflection at the layer for distances less than about 2,000 km and after only two reflections for distances greater than 2,000 but less than 4,000 km.

Figure 9 shows the geometry for one of the n hops between the transmitter and receiver. Let ϕ_n denote the angle of incidence of the waves at the layer, $2n\,\theta_n$ the angular distance between the transmitter and the receiver, and ψ_n the angle above the horizon with which the waves leave the transmitter or arrive at the receiver. Here n denotes the number of reflections at the layer which the waves make before arriving at the receiver. Let $R=6{,}371$ km denote the radius of the earth, $h=100$ km denote the virtual height of the layer and l the distance from the transmitter to the layer. The geometry of figure 9 gives:

$$\tan \phi_n = \frac{\sin \theta_n}{1-\cos \theta_n + \frac{h}{R}} \tag{3}$$

$$\psi_n = \frac{\pi}{2} - \phi_n - \theta_n \tag{4}$$

If, as before, D denotes the distance in kilometers between transmitter and receiver we have:

$$D = 222.1\, n\theta_n \text{ degrees} \tag{5}$$

[7] Phys. Rev., **21**, 554 (1926).
[8] BS J. Research **7**, 1083 (1931) RP390, or Proc. I. R. E., **20**, 286 (Feb. 1932).

The greatest distance for which waves may be reflected back to earth after a single reflection is determined by setting $\psi_1=0$ in eq 4 and substituting the resulting value of ϕ_1 in eq 3, whence:

$$\theta_{max}=\cos^{-1}\frac{R}{R+h}=10°5' \tag{6}$$

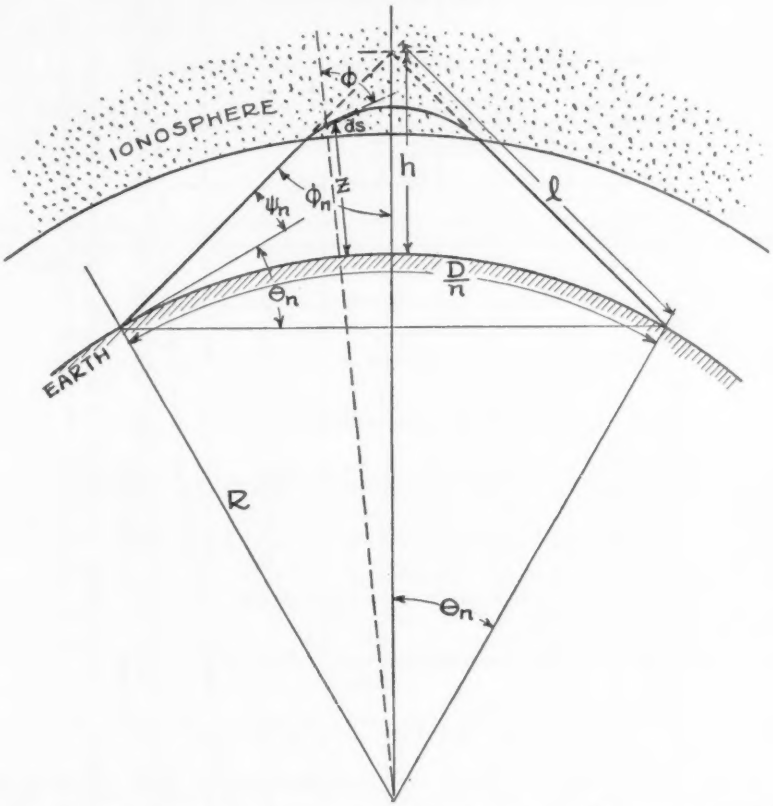

FIGURE 9.—*Geometry and the parameters concerned in theory of sky-wave propagation.*

In figure 10 ϕ_n and ψ_n are given graphically for one and for two reflections at the layer as a function of D. In general for n reflections we have the relations:

$$\phi_n(D)=\phi_1\left(\frac{D}{n}\right) \tag{7}$$

$$\psi_n(D)=\psi_1\left(\frac{D}{n}\right) \tag{8}$$

If we assume that the waves are reflected at the layer without absorption, then they will be received with an intensity:

$$F=\frac{C}{D}\sqrt{\overline{P_r(\psi_n)}}\,A_n=\frac{C}{2nl}\sqrt{P_r(\psi_n)} \tag{9}$$

so that:

$$A_n=\frac{D}{2nl}=\frac{\theta_n}{\sin\theta_n}\sin\phi_n\cong\sin\phi_n \tag{10}$$

where the attenuation factor A_n simply gives the reduction in field intensity due to traveling the inverse path distance as compared to the inverse great circle distance.

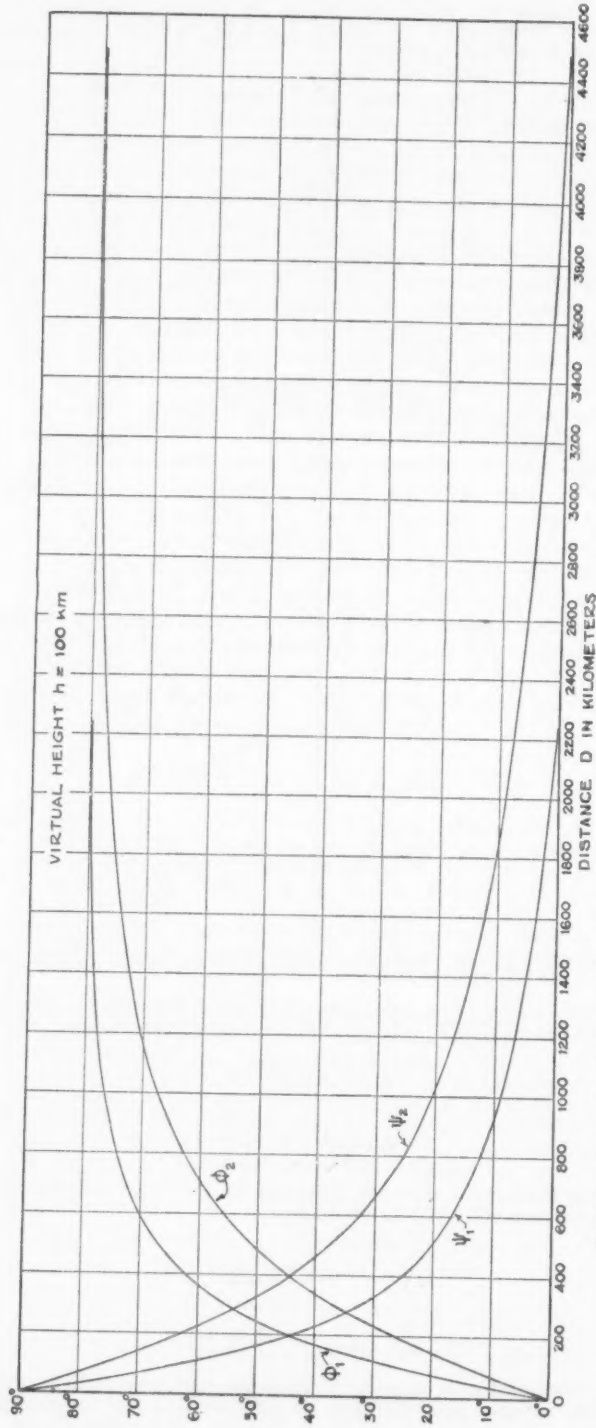

FIGURE 10.—*Variation with distance of two important parameters in the theory of sky-wave propagation.*

ϕ, the angle of incidence at the layer, and ψ, the angle above the horizon at which the radiation from the transmitter takes place.

It is possible to neglect the ratio $\frac{\theta_n}{\sin \theta_n}$ since θ_{max} for a 100-km layer is only 10°5′. Equation 10 then represents the attenuation factor for a single wave at a reflecting layer and is applicable for any finite distance between transmitter and receiver and for any number of reflections. It is evident that the succeeding reflections after the first will be weaker in the ratio $\sin \phi_n / \sin \phi_1$ and will be neglected in this discussion.

APPENDIX II. REFRACTION

The formula 10 was determined on the assumption that the waves were reflected without absorption at the layer. If we set Γ_n equal to the total attenuation along the ray path and γ equal to the attenutation per unit distance, then:

$$\Gamma_n = \int \gamma dS \tag{11}$$

where S denotes the distance along the ray path and the integration extends along the entire path. Now from the classical electromagnetic theory [9] we have the relations:

$$\gamma \sim \frac{Nv}{\mu\omega^2} \tag{12}$$

$$\mu^2 = 1 - \frac{CN}{\omega^2} \tag{13}$$

$$\cos \psi_n = \sin \phi \mu \left(1 + \frac{Z}{R}\right) \tag{14}$$

where N denotes the ionic density, v the collision frequency of the ions, μ the index of refraction, ω the angular frequency, Z the distance above the surface of the earth at any point along the ray path and C a constant. Results of ionization measurements during the solar eclipse of 1932 as reported by S. S. Kirby, L. V. Berkner, T. R. Gilliland, and K. A. Norton [10] indicate that the ionization during the daytime in the E layer consists mostly of heavy ions so that the modification of eq 13 due to the magnetic field of the earth may be neglected. At night this is probably no longer strictly true so that this constitutes one of the approximations of the theory. Equation 14 denotes the invariant for the ray path around a curved earth with ϕ denoting the angle which the ray makes with the vertical. From eq 3 and 4 we obtain:

$$\cos \psi_n = \cos \left(\frac{\pi}{2} - \phi_n - \theta_n\right) = \sin \phi_n \left(1 + \frac{h}{R}\right) \tag{15}$$

Combining eq 14 and 15 we obtain:

$$\sin \phi_n = \mu \frac{R+Z}{R+h} \sin \phi \cong \mu \sin \phi \tag{16}$$

Since there will be no absorption except in the layer, Z will not be much less than h throughout the range of integration so that we may safely make the approximation of setting the ratio $\frac{R+Z}{R+h} = 1$. The ray reaches the highest point and the greatest ion density, say N_0, when $\sin \phi = 1$ so that we obtain from eq 13 and 16:

$$N_0 = \frac{\omega^2}{C} \cos^2 \phi_n \tag{17}$$

At any point along the ray path we have:

$$dS = \frac{dZ}{\cos \phi} = \frac{\mu dZ}{\sqrt{\cos^2 \phi_n - \frac{CN}{\omega^2}}} = \frac{\mu dZ}{\cos \phi_n \sqrt{1 - \frac{N}{N_0}}} \tag{18}$$

[9] See e. g., P. O. Pedersen, The Propagation of Radio Waves, Copenhagen (1927).
[10] BS J. Research **11**, 829 (1933) RP629, and Proc. I. R. E. **22**, 247 (1934).

Substituting eq 12 and 18 into eq 10 we obtain:

$$\Gamma_n \sim \frac{n}{\omega^2 \cos \phi_n} \int \frac{N v \, d Z}{\sqrt{1-\frac{N}{N_0}}} = \frac{n}{\omega^2 \cos \phi_n} \int_0^{N_0} \frac{N v \, d N}{\frac{dN}{dZ}\sqrt{1-\frac{N}{N_0}}} \tag{19}$$

the first integration extending from the height for which $N=0$ to the height for which $N=N_0$. We will use the theorem of the mean to replace v by its mean value $\bar{v}$ and assume that N varies exponentially with the height so that:

$$\Gamma_n \sim \frac{n\bar{v}}{\omega^2 \cos \phi_n} \int_0^{N_0} \frac{dN}{\sqrt{1-\frac{N}{N_0}}} \tag{20}$$

Using the new variable $X=\frac{N}{N_0}$ we obtain:

$$\Gamma_n \sim \frac{n \bar{v} N_0}{\omega^2 \cos \phi_n} \int_0^1 \frac{dX}{\sqrt{1-X}} \sim n \bar{v} \cos \phi_n \tag{21}$$

Thus we obtain the result that the attenuation along the ray path [11] is proportional to the product of the number of reflections, the average collision frequency of the ions and the cosine of the angle of incidence at the layer. It is important to notice that the attenuation for the assumed exponential distribution of ion density is independent of the frequency. Since our results indicated no variation of received field intensity with frequency and since an exponential distribution of ion density is very probable because of the exponential absorption in the ionosphere of ultraviolet radiation from the sun, eq 21 very likely has the correct form. Combining the attenuation effects due to eq 10 and 21 we obtain the general expression for the attenuation factor for a ray after n reflections at the layer:

$$A_n = \sin \phi_n e^{-nk \cos \phi_n} \tag{22}$$

and the field intensity of this wave will be

$$F_n = \frac{C}{D}\sqrt{P_r(\psi_n)} \sin \phi_n e^{-nk \cos \phi_n} \tag{23}$$

where the radiated power is for the angle $\psi_n(D)$ and k is a constant independent of D and f but proportional to the average collision frequency of the ions along the ray path.

WASHINGTON, October 11, 1934.

[11] This same problem was solved in terms of somewhat less convenient variables in a paper by Shogo Namba, Proc. I. R. E., *21*, 238 (1933).

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